Development of a petrographic classification of fly-ash components from coal combustion and co-combustion. (An ICCP Classification System, Fly-Ash Working Group – Commission III.)

I. Suárez-Ruiz, B. Valentim, A.G. Borrego, A. Bouzinos, D. Flores, S. Kalaitzidis, M.L. Malinconico, M. Marques, M. Misz-Kennan, G. Predeanu, J.R. Montes, S. Rodrigues, G. Siavalas, N. Wagner

PII: S0166-5162(17)30279-3
DOI: doi: 10.1016/j.coal.2017.06.004
Reference: COGEL 2851

To appear in: *International Journal of Coal Geology*

Received date: 6 April 2017
Revised date: 15 June 2017
Accepted date: 17 June 2017

Please cite this article as: I. Suárez-Ruiz, B. Valentim, A.G. Borrego, A. Bouzinos, D. Flores, S. Kalaitzidis, M.L. Malinconico, M. Marques, M. Misz-Kennan, G. Predeanu, J.R. Montes, S. Rodrigues, G. Siavalas, N. Wagner , Development of a petrographic classification of fly-ash components from coal combustion and co-combustion. (An ICCP Classification System, Fly-Ash Working Group – Commission III.). The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Cogel(2017), doi: 10.1016/j.coal.2017.06.004

Development of a petrographic classification of fly-ash components from coal combustion and co-combustion. (An ICCP Classification System, Fly-Ash Working Group – Commission III)

I. Suárez-Ruiz[1*], B. Valentim[2], A. G. Borrego[1], A. Bouzinos[3], D. Flores[2], S. Kalaitzidis[3], M. L. Malinconico[4], M. Marques[2], M. Misz-Kennan[5], G. Predeanu[6], J.R. Montes[1], S. Rodrigues[7], G. Siavalas[8], N. Wagner[9]

[1]Instituto Nacional del Carbón (INCAR-CSIC). Ap.Co., 73. 33080-Oviedo. Spain.

[2]Instituto de Ciências da Terra, and Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, Portugal.

[3]Department of Geology, University of Patras, GR-265 04 Rio-Patras. Greece

[4]Department of Geology and Environmental Geosciences, Lafayette College, Easton, Pennsylvania USA.

[5]University of Silesia, Faculty of Earth Sciences, ul. Będzińska 60, 41-200 Sosnowiec, Poland.

[6]University Politehnica Bucharest, Research Center of Environmental Protection and Eco-friendly Technologies (UPB-CPMTE), Polizu St., 1, Sector 1, 011061, Bucharest, Romania.

[7]School of Earth Sciences, The University of Queensland, QLD 4072. Australia

[8]AfricaShell Global Solutions International, Integrated Charge Evaluation & Asset Geochemistry, Kessler Park 1, 2288 GL, Rijswijk, The Netherlands.

[9]Department of Geology, University of Johannesburg, Auckland Park, Johannesburg. South Africa.

* Corresponding author: Isabel Suárez-Ruiz, isruiz@incar.csic.es

Abstract

A new system for the microscopic classification of fly-ash components has been developed by the Fly-Ash Working Group, Commission III of the ICCP and is presented herein. The studied fly-ashes were obtained from the combustion of single coals of varied rank, coal blends, and coals blended with other fuels (biomass, petroleum coke), in different operating conditions and by means of different technologies. Microscopic images of the fly-ash samples were used to test the optical criteria proposed for classifying the fly-ash components.

The classification system developed is based on a small number of microscopic criteria, subdivided into six independent levels or categories, three of which are directed at whole particle identification on the basis of nature, origin and type of fly-ash particle, while the other three levels are directed at the smaller section identification on the basis of character, structure and optical texture of unburned carbons. To classify the inorganic components of the fly-ash, the criterion proposed is composition in terms of metallic / non-metallic character. To establish the classification criteria the petrographers involved in the work performed three successive round robins.

Evaluation of the results by using firstly descriptive statistics and then the criteria and parameters employed by the ICCP in their accreditation programs indicated that the classification of the fly-ash components was accurate and that there was only a minor bias. The main conclusion of this study was that the proposed criteria are valuable for identifying, and classifying fly-ash components and for describing the optical properties of fly-ash particles.

Keywords: Fly-Ash, Unburned carbons, Char, Petrography, Coal, Combustion, Biomass, ICCP, Fly-Ash Working Group

1. Introduction

Fly-ash is one of the residues generated during coal combustion and co-combustion (coal and other feed materials such as biomass, tires, wastes, etc.). Fly-ashes are fine particles that rise with the flue gases and are captured by electrostatic precipitators, bag-houses or cyclones before the flue gases are released to the atmosphere. Fly-ashes are composed of an inorganic fraction which is always the predominant one and an organic fraction, the so-called unburned carbons or fly-ash carbons, which may include: soot (carbon nanospheres); solid carbonaceous residue or char; and volatile organic compounds that may condense on the char surface to form pyrocarbon rims.

Fly-ash may be stored at the coal power plants, or they may be deposited in landfills and dumps resulting in extra management costs and negative environmental impact. For this reason, the best solution for the fly-ash is to be reused. Fly-ash can find applications in many fields such as the cement (Portland cement) and concrete industry, brick making industry, asphalt and concrete plants, waste treatment and soil stabilization, and geopolymers, among others. In all cases the different uses of fly-ashes depend on their composition, which is regulated by the ASTM C618 (2015) norm according to which fly-ash is grouped into classes C and F:

- Class C fly-ash is produced from combustion of lignite and subbituminous coal and has pozzolanic and some self-cementing properties. It generally contains more than 20% CaO, and alkali and sulfate contents are high in this C class of fly-ash;
- Class F fly-ash derives from combustion of medium and high rank coals (see ISO 11760, 2005 for coal classification). This fly-ash is pozzolanic in nature, and contains less than 20% CaO.

Because industrial classification of fly ash relies on inorganic matter, the inorganic fraction has received much more attention than the organic fraction (unburned carbons).

1.1. Unburned carbon from Fly-ashes

The unburned carbons from fly-ashes are also important because of their peculiar physico-chemical properties, which may also have an impact *e.g.*, on the air-entraining mixtures in concrete production and the alteration of concrete with time. In general, these unburned carbons have been characterized and investigated as a whole and although a few attempts have been made to classify the various forms of carbon, no comprehensive, useful or practical classification of fly-ash carbons has yet been developed. A comprehensive classification is necessary since the different fly-ash carbons have their own distinctive physico-optical and textural properties (Hower et al., 1995, 1996, 1999, 2000a,b, 2005a; Hower and Mastalerz, 2001; Suárez-Ruiz et al., 2006, 2007) and not all fly ash-carbons behave in the same way, for example in their capacity to retain trace elements (Hower et al., 1996, 1999, 2000b; Suárez-Ruiz et al., 2006, 2007) or when they are used as precursors for carbon materials (e.g., Hower et al., 2000a; Suárez-Ruiz et al., 2007; Girón et al., 2015). Other works report on the relationships between the surface area and the porosity of coal fly-ash and their carbon content (Schure et al., 1985). The nature of fly-ash carbons, their porosity, polarity, and optical properties, the influence of these properties on the adsorption of air-entraining admixtures (AEAs), and the size distribution of the carbons in relation to their surface area and accessibility in AEAs adsorption for both classes (C and F) of fly-ashes have been investigated by Baltrus et al. (2001); Gao et al. (1997); Külaots et al. (2004); Lee et al. (1999); Lyer and Stanmore (1995); Sarbak et al. (2004) among others. Fly-ash carbons have also been considered as being suitable for the development of sorbents (Akgerman and Zardkoohi, 1996; Li et al., 2006; Snape et al., 2004). The preparation of activated carbons, and in general the use of unburned carbons as precursors for other materials have been investigated by many authors (Baltrus, et al., 2001; Li et al., 2006). The main conclusion from all these research works is that the various fly-ash carbons have different properties which depend on their origin or feed fuel (Baltrus, et al., 2001; Külaots et al., 2004), and operating conditions during the process of combustion.

Interest in the development of a classification of fly-ash components dates back to the twenties of the last century when Newall and Sinatt (1924), Sinatt et al. (1927), and Sinnatt and Slater (1922) called the carbonaceous hollow spherical shells "cenospheres". However, only in the 1950's in the USA., was the importance of unburned carbons recognised again due to the growing interest in atmospheric pollution (Drinker and Hatch, 1954; Hamilton and Jarvis, 1963; McCrone and Delly, 1973), but the first fly-ash nomenclature schemes were not presented until the late 1970's (Fisher et al., 1978), and early 1980's (Ramsden and Shibaoka, 1982).

1.2. Chars and fly-ash microscopy

Over time a great amount of research and numerous petrographical studies on fly-ash and chars have been reported such as those by: Alonso et al. (2001); Álvarez et al. (1997); Alpern and Chauvin (1958); Alpern (1961, 1965); Alpern et al. (1957, 1960); Bailey et al. (1990); Bend (1989); Bend et al. (1992); Bengtsson (1986, 1987); Bourrat et al. (1986); Brunckhorst (1994); Cloke and Lester (1994); Crelling et al. (1992); Diessel and Wolff-Fischer (1987a,b); Goodarzi and Vleeskens (1988), Griest and Harris (1985); Gupta (2007); Hower et al. (1995, 1996, 1999, 2000a,b, 2005a); Hower and Mastalerz (2001); Jones et al. (1985a,b); Kleesattel et al. (1987); Lee and Whaley (1983); Lester et al. (1993, 1996, 2000, 2010); Lightman and Street (1968); Littlejohn (1967); McCrone and Delly (1973); Menéndez et al. (1993); Nandi et al. (1977); Oka et al. (1987); Petersen (1998); Phong-Anant et al. (1989); Ramsden and Shibaoka (1982); Rosenberg et al. (1996a,b); Shibaoka (1969a,b, 1985); Shibaoka et al. (1985, 1989); Skorupska et al. (1987); Street et al. (1969); Suárez-Ruiz et al. (2006, 2007); Suárez-Ruiz and Valentim (2007); Tang et al. (2005); Thomas et al. (1993a,b); Tsai and Scaroni (1984, 1987a,b); Valentim et al. (2006, 2009, 2011, 2013); Vleeskens and Malechaux (1986); Vleeskens and Nandi (1986); Vleeskens et al. (1988, 1993); Young et al. (1987); Yu et al. (2007), among others.

Two of the most complete classifications of chars (as a proxy of fly-ash components) by optical microscopy deserve to be highlighted. The first one was developed by Bailey et al. (1990) who established a char classification system that can be applied to coal combustion residues from subbituminous and bituminous coals. This classification was based on morphological, porosity and char wall thickness criteria. However, when this classification is applied to fly-ash it fails to cover all the residues found in fly-ashes, *e.g.*, *it* does not cover residues from the combustion of high-rank coals. The second classification is the very detailed ICCP Char Classification (Lester et al., 2000, 2010), which does not take into account the fact that the inorganic phases are the main components of fly-ash, and spinels, quartz and glassy material are all combined under the heading "mineroid" (Fig. 1A,B). Again, this classification does not cover all types of organic particles found in fly-ash, and does not fit well with some types of fly-ash carbons, *e.g.*, "inertoid" is a designation that includes either one char particle developed during pyrolysis, with a very low porosity (lower than 40%), unfused, isotropic, and probably derived from inertinite, and an anisotropic unburned carbon derived from the combustion of an anthracitic vitrinite (Fig. 1C,D).

Other pre-existing classifications specifically focused on fly-ash components (*e.g.*, Hower and Mastalerz, 2001; Hower et al., 2005a) are based on genetic and textural criteria, but either they are very difficult to handle due to the detailed descriptions and the use of numerical codes, or they are incomplete and do not cover all types of particles that can be found in fly-ash. For example in Hower and Mastalerz (2001: *vide* p. 1320) and Hower et al. (2005a: *vide* p. 653) the following classification is used:

(i) the first two categories ("Isotropic" and "Anisotropic carbons") are derived from the combustion of vitrinite and inertinite. However, "Inertinite" belongs to the third category, and particles derived from combustion of inertinite can also be isotropic or anisotropic carbons;

(ii) if inertinite is present, then it should be included in the "Uncombusted coal" category;

(iii) the "Petroleum coke" category should be included in "Other organics" like natural coke.

All of these classifications have the merit of providing a practical solution for fly-ash classification (*e.g.,*: Hower and Mastalerz, 2001; Hower et al., 2005a) by facilitating the development of a nomenclature and setting clear limits for the morphotype parameters (Lester et al., 2010). However, these classifications are directed at classifying the whole particle rather than for classifying the specific characteristics, textures and structures that fly-ash carbons show, thereby contributing only to a partial description of the characteristics of the unburned carbons. Consequently, the problem that needs to be addressed when classifying the fly-ash components is the following: Should the classification be directed towards the whole particle or, as in the case of analysis by means of a point counter on petrographic particulate pellets, should the classification be directed at the field or section at which the cross-hair is pointing? This is an important question because there are particles that contain sections that are, *e.g.*, porous and sections that are massive, fused sections and unfused ones, and the same problem affects anisotropy (see examples in Figs. 2 and 3).

On the other hand a classification needs to be easy to handle and, therefore, should be based on a few selected criteria related to the physico-optical properties of the fly-ash components. However, such a classification should include not only all the morphotypes of unburned carbons that may be found in fly-ashes as a result of the combustion of coal and blends, but also the unburned carbons derived from the co-combustion of coals and other materials.

Taking into consideration the points discussed above, a working group on " The identification and petrographic classification of components in fly-ashes" was created at the Annual Meeting of ICCP, Commission III, in 2005 in Patras (Greece), with the aim of identifying all the organic and inorganic components in fly-ashes by means of optical microscopy, and to establish an internationally accepted ICCP classification easy to handle and apply (ICCP, 2005).

During the 58th ICCP meeting, held in Bandung (Indonesia) in 2006, the ICCP Commission III members decided that the tasks of classification should begin with a round robin exercise to classify the fly-ash components following three main criteria (ICCP 2006) that should be applied in conjunction which each other (Suárez-Ruiz et al. 2006, 2007) as follows:

i)- Differentiate the organic and inorganic components;
ii)- In the case of the organic components, take into account their optical texture, fused or un-fused character, structure and morphology, and origin (coal, others), in that order;
iii)- In the case of inorganic components, classify them into two categories: metallic and non-metallic components.

The definitions of concepts such as "fused and unfused" character, and "porous and massive/dense" structure are based on the criteria established by the "Inertinite in Combustion WG" of the ICCP (http://www.iccop.org/workinggroup/inertinite-in-combustion/). The work of this group made an important contribution to establishing a unified criterion on the fused/unfused character and porous and massive/dense structure of the substance of sectioned char particles (Borrego et al., 1997), and also contributed to improving the definitions of borderline cases (such as mixed morphotypes, and solid inertoids) in the "ICCP Char Classification System" (Lester et al., 2000, 2010).

To reinforce the effectiveness of the classification, a glossary of pre-classification categories (Table 1) was defined during the 58th ICCP meeting (ICCP, 2006), and a classification of fly-ash components was established (Table 2).

2. Materials and methodology

2.1. Materials

The materials selected for the various exercises carried out by the Fly-Ash Working Group to improve the system of classification included fly-ash from the combustion of coals of a specific coal rank (covering the entire coal rank scale), fly-ash from the combustion of complex coal blends, and also fly-ash from the combustion of coal with other materials (co-combustion).

Participants in the various exercises were asked to identify the different components of the fly-ash in photomicrographs taken with a Leica camera coupled to a Zeiss Axioplan optical microscope using the corresponding software for image analysis, in reflected white light, polarized light and with a 1 λ retarder plate, using oil immersion objectives of ×50 magnification and ×10 oculars. The images of specific fly-ash components were taken at two different positions on the microscope by rotating the stage 360° to see whether the particles developed anisotropy. In addition, taking into account that the identification had to be carried out at two levels, *i.e.,:* specific particle section level and whole particle level, all the images contained a cross, an arrow or a square indicating the particular field section to be identified. This was particularly important in the case of particles with two components or very different optical characteristics.

2.2. Methodology

The methodology proposed for developing the classification of fly-ash components included a set of three round robin exercises carried out in successive years. The first exercise was developed in 2007. This exercise that had to be performed in approximately 2 hours, consisted of a folder containing 210 pictures – 70% fly-ash carbons and 30% inorganics -, selected from a total of 2000 digital photomicrographs of fly-ashes derived from the combustion of pulverized feed coals and coal blends covering the entire coal rank used in European power plants, in some cases containing also petroleum and natural coke. For the analysis two pictures of each fly-ash component were included in the exercise, showing the anisotropy/isotropy of the particle. Each section of the particle to be identified and classified had been previously marked with a cross or an arrow to discriminate, for example, between particles with two components or two very different optical characteristics (Fig. 2).

The first step of the 2007 exercise was to apply the criteria based on the optical and textural properties of the components as well as their origin in order to classify the inorganic and organic components in the fly-ash by means of optical microscopy. For this purpose two main categories based on the nature of the fly-ash components were established: organic components (fly-ash carbons or unburned carbons), and mineral matter.

The criteria used to identify the fly-ash carbons were: their optical texture (whether they had an isotropic or anisotropic character); their fused, unfused or partially fused character; the structure and morphology of the fly-ash carbons (dense and massive particles *versus* porous and vesiculated, irregular *versus* spherical (*e.g.*, crassispheres, tenuispheres); their origin, *i.e.*, whether carbons were derived from coal or from some other provenance such as petroleum coke. In addition, fly-ash carbons from coal could be differentiated according to the coal rank from which they were derived, and according to the precursor macerals from which they originated.

To classify the inorganic fraction and taking into account the limitations of petrographic methods in reflected light, the first step was to separate the inorganic fraction into two categories: metallic and non-metallic inorganic components. Moreover, it was suggested that the conventional criteria such as physico-optical properties (*e.g.*, color, structure and morphology, crystallinity, etc.) should be used in combination with the categories previously reported by Hower et al. (2005a). Based on the results of the 2007 exercise (discussed below), a new round robin exercise was proposed for 2009.

The second exercise in 2009 was prepared using images of fly-ash components obtained from the combustion and co-combustion of coal, biomass and coal and biomass in conditions of Pulverized Coal Combustion (PCC) and Fluidized Bed Combustion (FBC). The images were taken in the same conditions as those of the 2007 exercise. In this exercise, however, the participants had to identify and classify 279 organic and inorganic components shown in photomicrographs selected from a pool of about 1000 digital images. The participants were asked to follow the same criteria as those of the 2007 exercise (except for the partially fused qualifier that was removed) using the following sequence of classification: i) optical texture (anisotropic / isotropic); ii) fused / unfused character; iii) structure and morphology of the fly-ash carbons (massive particles, vesiculated, and with porosity, irregular, and similar features); and iv) origin. The participants in the exercise were also requested to identify and classify inorganic components (following Hower et al., 2005a) on the basis of their: i) metallic / non-metallic character; ii) physic-optical properties; iii) undifferentiated inorganic components (due to the small size of the inorganic material or the poor resolution of the microscope).

From the 2009 results, and the remarks and suggestions received, the classification of the fly-ash components was then simplified and organized into 6 levels of component identification: 3 levels relating to the identification of a specific field within a particle (e.g., Figs. 2, 4C-D, 5) and 3 levels relating to the classification of the whole fly-ash particle (Fig. 3). Thus:

- Level # 1 addresses the classification of the whole particle and corresponds to the *nature of the particles*:

  i) Organic Components, *i.e.*, fly-ash carbons (unburned carbons); and,

  ii) Inorganic Components.

- Level # 2 addresses the identification of the particle field which is marked with a square instead of a cross or an arrow and is the *optical character* that may be:

  i) Fused. Fused character is described as a section of a particle that appears with a rounded or sub-rounded morphology, and evidences swelling and /or caking, and an absence of sharp edges due to physico-chemical changes during combustion or heating; or,

  ii) Unfused. Unfused character corresponds to a section of a particle without any of the characteristics described above. The particle section is flat, has sharp edges, and can exhibit a cell-like structure (original or newly formed), or a "glove finger" type structure.

- Level # 3 of this classification addresses the *optical structure* in the particle field identified. This *optical structure* can be:

  i) Dense (massive). A Dense / Massive structure is defined as a section of a particle without any porosity or devolatilization pores; or,

  ii) Porous and vesiculated. A Porous / Vesiculated structure is a section of a particle with pores resulting from thermal devolatilization (distorted pores, coalescent pores). A porous structure can be a field particle section that still retains its original porosity (cell/cavity structure).

(*Note: the corresponding descriptions of "fused" or "unfused" character, dense (massive) or porous and vesiculated were also included in the classification to avoid misunderstanding*)

- Level # 4, *optical texture*, also addresses a specific field marked on the fly-ash component:

i) Isotropic. Isotropic texture is the section of a particle that does not modify its color or color intensity when it is rotated 360°; or,

ii) Anisotropic. Anisotropic texture is a section of a particle that modifies its color or color intensity when it is rotated 360°.

- Level # 5 of the classification corresponds to the *origin*, with several possibilities: unburned carbons from coal, biomass, petroleum coke, among others (*e.g.*, tires). This Level of classification addresses the whole particle.
- Level # 6 refers to the *type of particle*. In this case it is necessary to consider the whole particle, applying *the ICCP Char Classification* (Lester et al., 2000, 2010).

The advantage of the proposed classification by levels is that *Levels* are independent and the petrographers can classify fly-ash components by selecting the specific level or levels of their particular interest. For the inorganic components the classification was the same as that described in the 2007 and 2009 exercises.

This new classification by levels, was checked in a new round robin exercise, carried out in 2011 at the ICCP Meeting in Porto (Portugal). In this case 25 images of fly-ash components (in two different positions) were selected. As usual, the participants had to classify each image using the first four levels (from level # 1 to level # 4), levels #5 and # 6 being optional.

The results from each exercise (1^{st}, 2^{nd} and 3^{rd}) were evaluated to check the effectiveness and accuracy of the proposed criteria for the identification and classification of Fly-Ash Components by the participants in the various exercises. In the evaluation basic descriptive statistics were applied such as *mean (average), median* and *mode values*, and *level of agreement* between the responses of the participants with respect to the established criteria.

2. Results and Discussion

3.1. First fly-ash classification round robin exercise (year 2007)

The results from twelve participants, representing seven laboratories and seven countries (Greece, Poland, Portugal, Romania, South Africa, Spain, and the USA) showed good agreement in the classification of the organic components (>80%). That is, most of the images of organic components that had to be analyzed showed a level of agreement among the participants of above 80% using the average, median and mode values, Table 3). However, poor agreement was obtained in the classification of inorganic components. The average, median and mode values were below 75% (Table 3) which meant that the analysts' performances in identifying and classifying the inorganic fraction was not satisfactory in this round robin.

In relation to optical texture (with two qualifiers: isotropic/anisotropic) the participants had found that 56% of the fly ash carbons were anisotropic and 44% were isotropic (see amount of particles assigned to each qualifier in Table 3). The participants showed a high level of agreement between 80-100% (> 80%, see agreement classes in Table 3) in the assignments for 65% of the carbons with respect to these criteria.

As for structure (dense/porous) and origin (coal/other) the participants also showed a high level of agreement (above 80%, see average, median and mode values in Table 3 for analysts' performance), while optical character (fused/unfused) resulted in a low level of agreement (< 80%; Table 3), (examples in Fig.5). For optical character the participants in the round robin decided that 40% of the particles were fused carbons; 31% were unfused carbons and 29% were classified as partially fused carbons (see amount of particles assigned to each qualifier in Table 3). The level of agreement between the participants in the responses for this criterion is low. 35 % of the carbons were classified with a level of agreement between 80 and 100%; 29% with a level of agreement between 65 and 80%; 31% of the images with a level between 50 and 65% and finally 5% of the images with a level of agreement lower than 50% (see agreement classes in Table 3). The "partially unfused" qualifier was responsible for the worst results (see analysts' performance in Table 3) of the optical character criterion.

As mentioned above, most of the inorganic components were classified with a low level of certainty, since only thirty percent of the pictures (see agreement classes in Table 3) showed a level of agreement above 80%, 73% being the average, median and mode values (see analysts'performance in Table 3). This was because the inorganic components could be classified according to three qualifiers (metallic, non-metallic and undifferentiated) and because of the lack of experience of some analysts who were not able to assign the inorganics to the category of metallic or non-metallic, and classified the ambiguous inorganic particles in the category of undifferentiated inorganics (examples in Fig. 6).

The general conclusion drawn from the 2007 exercise was that the proposed criteria for identifying and classifying the fly-ash components were: correct, effective and easily applicable (TSOP Newsletter # 25/3, 2008. http://www.tsop.org and Minutes of Commission III, ICCP Meeting, Victoria 2007). However, it was considered that the "partially fused" qualifier should be removed in the next round robin exercise when using fly-ashes from combustion and co-combustion. The same proposal was made for the third qualifier (undifferentiated inorganics) used for the identification of inorganic components.

3.2. Second fly-ash classification round robin exercise (year 2009).

The main objective of this exercise was to check the criteria established for classifying the fly-ash components in fly-ashes derived from combustion of coals, co-combustion, and combustion of biomass in European and US power plants in conditions of pulverized coal combustion (PCC), fluidized bed combustion (FBC), stoker boilers, and heating boilers. Some feed fuels also contained petroleum coke. For this exercise the criteria were simplified as follows:

- Classification of fly-ash components based on their nature: 1) *Organic Components*: fly-ash carbons (unburned carbons); and 2) *Inorganic Components*.
- Classification of fly-ash carbons according to: i) Their *optical texture*: *isotropic / anisotropic texture*; ii) *Character*: *fused/unfused/partially fused*; iii) *Structure: dense/massive vs. porous/vesiculated*; iv) *Origin*: *coal/biomass/other*.
- Classification of *Inorganic components* according to: i) Their *character*: *metallic/non-metallic*; ii) *undifferentiated*.

Although in this proposal the qualifiers "partially fused" for unburned carbons and "undifferentiated" for inorganics were still kept, it was recommended that they should not be used and that the sections and particles observed should be assigned to the "fused" or "unfused" and to the "metallic" or "non-metallic" qualifiers.

This exercise was performed on 279 images (165 of unburned carbons and 114 of inorganics) and the identification and classification had to be performed following the pre-established criteria on the section of the particle marked with a cross or an arrow (examples in Figs. 2, 4, 7). This was particularly important in the case of particles with two components or very different optical characteristics. A statistical evaluation of the results revealed an improvement in the identification of inorganic components with respect to those obtained in the exercise of 2007. On the other hand, there was a good agreement in the identification and classification of the organic components with average, median and mode values of 81%, 80% and 78%, respectively (see analysts' performance in Table 4); and for inorganic components in all cases > 80% (Table 4) indicating that most participants managed to assign the mineral matter to the metallic or non-metallic categories successfully.

In the case of the fly-ash carbons, in this exercise high agreement (≥ 80%) was achieved in optical texture (isotropic/anisotropic), character (fused/unfused) and origin (coal/other) (see average, median and mode values for these qualifiers in analysts' performance of Table 4 and Fig.7). As in the previous case the participants classified most of the fly-ash carbons as fused or unfused, avoiding the qualifier "partially fused" (see amount of particles assigned to each qualifier in Table 4). However, the worst level of agreement (<75%) was achieved for the "structure" criterion (average, median and mode values for structure in analysts' performance of Table 4). This was due to the type of marker used. When an arrow or a cross is used as a marker of a specific field particle that is to be classified, those markers actually indicated only a point and participants were required to look at the whole particle. This led to bias in the assessment of the results and lowered the corresponding level of agreement on the porous/massive qualifiers (Table 4). In addition the degree of difficulty in identifying the particles largely increased with respect to the 2007 exercise. However, despite this, the 2009 results confirmed again that the criteria proposed for identifying and classifying the fly-ash components were correct, effective and easily applicable to the different combustion fly-ashes.

Despite the acceptable results, in the discussions of the Gramado 2009 ICCP Meeting, the removal of "cenosphere, network", and similar terms belonging to the ICCP Char Classification System (Lester et al., 2000, 2010) for the classification of fly-ash was suggested. In addition a request was also made for the modification of the pre-classification and the setting up of several different, and independent levels: level # 1 for the nature of the fly-ash components; level # 2 for the optical texture, character and structure/morphology; level # 3 for the type of particle (at this point ICCP char classification can be applied); level #4 for the origin of the fly-ash carbons; level # 5 for the rank of the coal-derived carbon; and, level # 6 for "other". During the Belgrade ICCP Meeting (2010) a set of new modifications was requested for the fly-ash classification including: i)- to improve the level of the description by indicating that some of these levels are only concerned with particle surface identification (as in the case of maceral analysis), ii)- to keep one level for classifying the total particle (as in the ICCP Char Classification) by describing the characteristics to be analyzed including graphical examples, and iii)- to replace the cross / arrow by an empty square on the specific particle surface to be classified. In addition it was also decided not to use the qualifiers "partially fused" and "undifferentiated" for the character of unburned carbons and the inorganics respectively.

3.3. Third fly-ash classification round robin exercise (year 2011).

A new round robin exercise was proposed for the years 2011-2012. In this exercise for which 25 pictures of fly-ash components were used the independent criteria to be successively applied were structured on 6 levels as follows (Table 5; http://www.iccop.org/documents/atlas-of-fly-ash-occurrences.pdf): with 3 levels addressing the identification of the small local particle field marked with a square (Fig. 8) for particle surface identification, and 3 levels directed at the whole particle in the image (see definitions in Table 1).

Level # 1 is directed at the whole particle and is based on the *Nature* of the particles: i) *organic components*: fly-ash carbons (unburned carbons); or, ii) *inorganic components*.

Level # 2 is directed at particle field identification, and refers to the *Optical character* of the field section which may be: i) *fused*; or, ii) *unfused*.

Level # 3 is directed at particle field identification and corresponds to the *Optical structure* which may be: i) *dense / massive*; or, ii) *porous / vesiculated*.

Level # 4 is directed at particle field identification and corresponds to the *Optical texture* which may be: i) *isotropic*; or, ii) *anisotropic*.

Level # 5 is directed at the whole particle and refers to the *Origin* of the particle that may be: i) *coal*; ii) *biomass*; iii) *petroleum coke*; and; iv) *others* (such as tires, etc.)

Level # 6 is directed at the whole particle and corresponds to the *Type of particle*. To describe the Type of particle it is necessary to apply the ICCP Char Classification System (http://www.iccop.org/workinggroup/inertinite-in-combustion/) published under Lester et al. (2000, 2010)

In 2011 during the Porto ICCP Meeting all the participants at the meeting, most of them inexperienced in fly-ash microscopy were asked to perform an exercise on the classification of fly-ash components during a session lasting 25 minutes (one minute per exercise slide) and in 2012, the participants in the working group were also requested to perform the same exercise. The assessment of the results obtained from the 2011 round robin exercise including all the suggested modifications to the pre-existing classifications showed that the total analysts' performance of the WG Non-members was lower than that of the WG members, *i.e.*, they obtained lower mean, median and mode values, which is explained by the lack of experience of most of the non-members of this ICCP working group with this type of round robin and with this topic. Consequently the final assessment of the results was only carried out using the results provided by the Fly-Ash Classification Working Group members. In this case there was excellent agreement (96%, 96%, 100% for the average, median and mode values, respectively) for the identification and classification of fly-ash components with regard to the *nature* criterion (analysts' performance in Table 6, and Fig. 8). The criteria for the classification of the fly-ash carbons namely *character*, *structure*, *optical texture* and *origin* showed levels of agreement of 62%, 70%, 78%, 56% for the average value; 64%, 72%, 80%, 56% for the median value and, 60%, 72%, 80% and 60% for the mode value, respectively, with the best corresponding to optical texture (*isotropic/anisotropic* fly-ash carbon) and the poorest to *origin* (Table 6). The positive trend found in the level of agreement for the various criteria used in the identification and classification of the fly-ash components may be due to the small number of images used in this exercise. Additionally, it was concluded that an increase in the number of exercises to be performed would not increase the level of agreement. Level # 6 (*Type of particle* in the ICCP Char Classification) was not included in the results assessment because it was not mandatory.

3.4. Precision and bias of the analysts: suitability of the proposed criteria for fly-ash component classification.

To obtain a better idea of the performance of the analysts in the identification and classification of the fly-ash components using the proposed criteria it was decided to apply ICCP statistics (http://www.iccop.org/accreditation/statistical-evaluation-in-detail/). These statistics are usually applied to the Accreditation Programs of the ICCP and they are based on the mean of the group of analysts and on the standard deviation against the group means (multiple standard deviations). This enabled an assessment of the accuracy and bias of the analysts in the identification and classification of the fly-ash components.

The parameters used for this evaluation (whose definitions and meanings are in the website mentioned above) were the Group Mean (GM), the Group Standard Deviation (GSD), the Signed Multiple of the Standard Deviation (SMSD) calculated against the GM and the GSD, and the Averaged Signed Multiples of the Standard Deviation (ASMSD). This latter parameter is a measure of the bias of the group means and indicates the degree of consistency of an analyst. Other parameters included in this evaluation were the Unsigned Multiple of the Standard Deviation (UMSD) which is the absolute value of SMSD, and the corresponding Average Unsigned Multiple of the Standard Deviation (AUMSD). This parameter is an indicator of the dispersion of the group means and a measure of the accuracy of the analyst. If the dispersion with respect to the mean values (AUMSD) is below 1.5 (value used as a cut-off in the ICCP Accreditation Programs), the results are acceptable.

According to this, the GM, GSD, the SMSD (and UMSD) were calculated taking into account each qualifier of the various established criteria and also the AUMSD and ASMSD for each participant as can be seen in Tables 7 and 8. The results in Table 8 show that all the analysts had an AUMSD value <1.5 and in all cases the ASMSD indicate a minor bias (± <0.5).

The values of AUMSD for all the analysts and the classification criteria indicate that the data offer a consistent basis for assessing the quality of the selected criteria and the procedure followed for classifying the components of fly-ash.

Taking into account the results obtained a final classification was established as reported in http://www.iccop.org/documents/atlas-of-fly-ash-occurrences.pdf and shown in Table 5. This scheme is easy to handle and permits a rapid identification and classification of the components of fly-ash produced by the combustion of coals and other fuels.

3.5. Level # 1 of the Petrographic Classification of Fly-ash Components: Disambiguation.

The "Petrographic Classification of Fly Ash Components" described here and developed by the corresponding Working Group in Commission III of the ICCP (Suárez-Ruiz et al., 2015) is meant to be universal. However, coal is a heterogeneous material and coal fly-ash reflects this heterogeneity. Due to this heterogeneity, as well as the combustion process and conditions, the fly-ash organics and inorganics and their associations may be grouped in general and in more or less specific terms, but there are ambiguous situations.

Level #1 of the "Petrographic Classification of Fly Ash Components" is described as being mainly directed at whole particle identification and corresponds to the nature of the particles: i) Organic Components (unburned carbons); and ii) Inorganic Components. This means that a particle at level # 1 is classified as a whole. However, it may be a particle that is totally (100%) composed of carbonaceous matter or totally (100%) composed of inorganic matter (Fig. 9A,B). In such cases it is very easy to decide and classify the particle from the point of view of its "nature". Nevertheless, there are mixed organic-inorganic particles with a variable volume % of either component (organic and inorganic, Fig. 9 C-F). The assignation of "nature" to this kind of particles may be more problematic if the whole particle is being considered. In this case and in a quantitative analysis involving the use of a point counter the "nature" assignment should be carried out with respect to the point that is marked by the cross-hair. If the cross-hair is pointing at carbonaceous material, then the nature will be organic, if the cross-hair is pointing at mineral matter, then the nature will be inorganic.

4. Conclusions

A new system for the petrographic classification of fly-ash components has been developed by the Fly-Ash Working Group, Commission III of the ICCP. This classification system is based on a small number of easily applicable microscopic criteria that were established after three round robins exercises successively performed by petrographers involved in this task.

The fly-ashes used in the various round robins were obtained from the combustion of single coals of varied rank, coal blends, and coals blended with other fuels (biomass, petroleum coke) using different operating technologies and conditions (pulverized coal combustion, fluidized bed combustion, stoker boilers, and heating boilers). Images taken of the fly-ash components were used in a series of round robin exercises.

After the evaluation of results from the first two exercises (performed in 2007 and 2009) using descriptive statistics, three main issues were raised. The first one was to decide on how to apply the pre-selected criteria: on the whole particle or on a section of the particle. This work has demonstrated that when particles are being classified by microscopic examination it is necessary to establish first whether the classification should take into account the whole particle or the classification should be based on the field section on which the cross-hair is falling. This distinction is important because most of the particles to be classified, particularly organic particles, like fly-ash are heterogeneous, and displaying several optical properties in the same particle.

The second and third issues were to reduce the number of qualifiers included to a specific criterion to improve the accuracy and performance of the analysts and ensure a similar quality of results. Therefore, the "partially fused" and "undifferentiated inorganics" qualifiers were removed from the criteria "character of unburned carbons" and "inorganics", respectively.

The initial criteria proposed for classifying the fly-ash carbons in the first two round robins were then modified leaving only the appropriate criteria that best describe the optical characteristics of an unburned carbon. These criteria, for fly-ash carbons, are independent of each other and were subdivided into 6 levels of identification, three directed at the whole particle (nature, origin and type of fly-ash component) and three directed at a specific particle field (character, structure and optical texture of the fly-ash carbons). Each criterion contains two qualifiers with the exception of "origin" which has three qualifiers taking into account the different feed fuels. For inorganics, considering the limitations of optical microscopy, the classification criteria are based on their composition with two qualifiers: metallic and non-metallic.

The criteria for classifying the fly-ash components were tested, in 2011, in a third round robin exercise and after the application of two evaluation procedures, the second one based on the statistical parameters used in the existing ICCP accreditation programs (www.iccop.org), yielded the most satisfactory results for classifying the components with a good accuracy and only a minor bias. Therefore, the proposed criteria were found to be valuable for identifying, classifying and describing the optical properties of the components of fly-ash.

Acknowledgments

- Programa de Acções Integradas Luso-Espanholas 2010/2011, Conselho de Reitores da Universidade do Porto (CRUP), Acção Integrada Luso-Espanhola E65-10. Portugal.
- Subprograma de Acciones Integradas. Ministerio de Ciencia y Innovación, PT2009-0122. Spain.
- Faculdade de Ciências da Universidade do Porto (Portugal).

- Instituto Nacional del Carbón (INCAR-CSIC, Oviedo, Spain).
- The conveners of the Fly-Ash Working Group also thank the participants who generously participated in the Working Group Session exercise at the 2011 ICCP Meeting held at Porto (Portugal).

References

Akgerman, A., Zardkoohi, M., 1996. Adsorption of Phenolic Compounds on Fly Ash. Chem. Eng. Data 41, 185-187.

Alonso, M.J.G., Borrego, A.G., Alvarez, D., Parra, J.B., Menéndez, R. J., 2001. Influence of pyrolysis temperature on char optical texture and reactivity. Journal of Analytical and Applied Pyrolysis 58-59, 887-909.

Álvarez, D., Borrego, A.G., Menéndez, R., 1997. Unbiased methods for the morphological description of char structures. Fuel 76, 1241-1248.

Alpern, B., Courbon, P., Plateau, G., Tissandier, G., 1957. Etude au microscope d'echantillons pris dans une flame de charbon pulverise. In: Essais sur le Mécanisme de Combustion du Charbon – 1e Série (CMC1), Ijmuiden 1957. 9 pp. (Document Nº F17/b/5).

Alpern, B, Chauvin, R., 1958. Application des méthodes de la microscopie par réflexion à l'étude de la combustion des boulets. Rev. Ind. Minér., Nr. Spéc. 15 Juillet 1958: 210-218. (C.R. Colloq. International de Pétrologie Appliquée des Charbons, Paris – 1957).

Alpern, B., Courbon, P., Plateau, G., Tissandier, G., 1960. Microscopic examination of samples taken from a pulverized-fuel flame. Journal of the Institute of Fuel 33, 399-402.

Alpern, B., 1961. Etude microscopique du mode de combustion des houilles. Centre d'Études et Recherches des Charbonnages de France. Verneuil-en-Halatte. (Document Intérieur CHERCHAR Nº. 1185).

Alpern, B., 1965. Application de la microsonde électronique a l'étude des cendres volantes et des minéraux des charbons. 13 pp. Centre d'Études et Recherches des Charbonnages de France. Verneuil-en-Halatte. (Document Intérieur CHERCHAR Nº. 1562).

ASTM C618-15, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, ASTM International, West Conshohocken, PA, 2015, www.astm.org

Bailey, J.G., Tate, A., Diessel, C.F.K., Wall, T.F., 1990. A char morphology system with applications to coal combustion. Fuel 69, 225-239.

Baltrus, J.P., Wells, A.W., Fauth, D.J., Diehl, J.R., White, C.M., 2001. Characterization of Carbon Concentrates from Coal-Combustion Fly Ash. Energy Fuels 15, 455-462.

Bend, S.L., 1989. Coal Characterisation and Combustion. University of Newcastle upon Tyne, PhD Thesis.

Bend S.L., Edwards I.A.S., Marsh H., 1992: The influence of rank upon char morphology and combustion. Fuel 71, 493-501

Bengtsson, M., 1986. Combustion behaviour for a range of coals of various origins and petrografic composition. The Royal Institute of Technology. Department of Heat and Furnace Technology, Stockholm, Sweden. Ph.D. Thesis.

Bengtsson, M., 1987. Combustion behaviour for a coal containing a high proportion of pseudovitrinite. Fuel Processing Technology 15, 201-212.

Borrego, A.G., Alonso, M.J.G., Alvarez, D., Clift, D., Flores, D., Hall, K., Kruszewska, K., Kwiecinska, B., Lester, E., Marques, M., Panaitescu, C., Petersen, H., 1997. "Classification of Char Optical Texture. ICCP System 1996". Report of the 1997 Round Robin microscopy exercise on a medium rank inertinite-rich coal char. International Committee for Coal and Organic Petrology (ICCP), Inertinite Combustion Working Group (INCWG97), 12 pp.

Bourrat, X., Oberlin, A., Escalier, J.C., 1986. Microtexture and structure of semi-cokes and cokes. Fuel 65, 1490-1500.

Brunckhorst, L., 1994. A method for mounting, grinding and polishing very small laser-hit coal grains for microscopy and image analysis. Fuel 73 (3): pp. 463-464.

Cloke, M., Lester, E., 1994. Characterization of coals for combustion using petrographic analysis: a review. Fuel 73, 315-320.

Crelling, J.C., Hippo, E.J., Woerner, B.A., West Jr., D.P., 1992. Combustion characteristics of selected whole coals and macerals. Fuel 71, 151-158.

Diessel, C.F.K., Wolff-Fischer, E.M., 1987a. Coal and coke petrographic investigations into the fusibility of Carboniferous and Permian coking coals. International Journal of Coal Geology 9, 87-108.

Diessel, C.F.K., Wolff-Fischer, E.M., 1987b. Proposal for a classification of combustion residues. Communication to the International Committee for Coal and Organic Petrology (ICCP) Meeting, Beijing, 1987.

Drinker, P., Hatch, T., 1954. Industrial dust. 2nd ed., New York: McGraw-Hill (330 West 42nd St.), 1954. 401 pp.

Fisher, G.L., Prentice, B.A., Silberman, D., Ondov, J.M., Bierman, A.H., Ragaini, R.C., McFarland, A.R., 1978. Physical and morphological studies of size-classified coal fly ash. Environmental Science and Technology 12, 447-451.

Gao, Y.-M., Shim, H.-S., Hurt, R.H., Suuberg, E.M., Yang, N.Y.C., 1997. Effects of Carbon on Air Entrainment in Fly Ash Concrete: The Role of Soot and Carbon Black. Energy & Fuels 11, 457-462.

Girón, R.P., Gil, R.R., Suárez-Ruiz, I., Fuente, E., Ruiz, B., 2015. Adsorbents/catalysts from forest biomass fly ash. Influence of alkaline activating agent. Microporous and Mesoporous Materials 209, 45–53.

Goodarzi, F., Vleeskens, J.M., 1988. Reactivity of bituminous-semianthracitic coals: a reflected light study of their combustion residues (fly ash). Journal of Coal Quality 7, 80-85.

Griest, W.H., Harris, L.A., 1985. Microscopic identification of carbonaceous particles in stack ash from pulverized-coal combustion. Fuel 64, 821-826.

Gupta, R., 2007. Advanced Coal Characterization: A Review. Energy & Fuels 21, 451-460.

Hamilton, E.M., Jarvis, W.D., 1963. The identification of atmospheric dust by use of the microscope. Central Electricity Generating Board, Research and Development Department, London, England. March 1963. 32 pp.

Hower, J.C., Mastalerz, M., 2001. An approach toward a combined scheme for the petrographic classification of fly ash. Energy and Fuels 15, 1319-1321.

Hower, J.C., Finkelman, R.B., Rathbone, R.F., Goodman, J., 2000a. Intra- and inter-unit variation in fly ash petrography and mercury adsorption: examples from a western Kentucky power station. Energy & Fuels 14, 212-216.

Hower, J.C., Maroto-Valer, M., Taulbee, D.N., Sakulpitakphon, T., 2000b. Mercury Capture by distinct fly ash carbon forms. Energy & Fuels 14, 224-226.

Hower, J.C., Rathbone, R.F., Graham, U.M., Groppo, J.G., Brooks, S.M., Robl, T.L., Medina, S.S., 1995. Approaches to the petrographic characterization of fly ash. Proceedings of 11th International Coal Testing Conference, Lexington, KY, May 10-12, 49-54.

Hower, J.C., Rathbone, R.F., Robertson, J.D., Peterson, G., Trimble, A.S., 1999. Petrology, mineralogy and chemistry of magnetically-separated sized fly ash. Fuel 78, 197-203.

Hower, J.C., Thomas, G.A., Clifford, D.S., Eady, J.D., Robertson, J.D., Wong, A.S., 1996. Petrography and chemistry of high-carbon fly ash from the Shawnee Power Station, Kentucky. Energy Sources 18, 107-118.

Hower, J.C., Suárez-Ruiz, I., Mastalerz, M., 2005a. An approach toward a combined scheme for the petrographic classification of fly ash: revision and clarification. Energy & Fuels 19, 653-655.

Hower, J.C., Thomas, G.A., Mardon, S.M., Trimble, A.S., 2005b. Impact of co-combustion of petroleum coke and coal on fly ash quality: case study of a Western Kentucky power plant. Applied Geochemistry 20, 1309-1319.

International Committee for Coal and Organic Petrology (ICCP), 2005. Minutes of Commission III, Industrial Applications of Coal Petrology 57th ICCP meeting, Patras (Greece) 2005. ICCP News 36, p.37.

International Committee for Coal and Organic Petrology (ICCP), 2006. Minutes of Commission III, Industrial Applications of Coal Petrology58th ICCP Meeting, Bandung 3-9 September 2006. ICCP News 39, p. 38.

ISO 11760:2005. Classification of coals. International Organization for Standardization, 1st edition, Geneva, Switzerland, 9 pp.

Jones, R.B., McCourt, C., Morley, C., King, K., 1985a. Maceral and rank influence on the morphology of coal char. Fuel 64, 1460-1467.

Jones, R.B., Morley, C., McCourt, C.B., 1985b. Maceral effects on the morphology and combustion of coal char. In Proceedings of the “1985 International Conference on Coal Science”. Sydney, 28-31 October, 669-672.

Kleesattel, D., Benson, S.A., Jones, M.L., McCollor, D.P., 1987. In Extended Abstracts, Joint Fall Meeting, Western States and Japanese Sections, The Combustion Institute, Pittsburgh, 1987, 122-125.

Külaots, I., Hurt, R.H., Suuberg, E.M., 2004. Size distribution of unburned carbon in coal fly ash and its implications. Fuel 83, 223-230.

Lee, K.T., Bathia, S., Mohamed, A.R., Chu, K.H., 2006. Optimizing the specific surface area of fly ash-based sorbents for flue gas desulfurization. Chemosphere 62, 89-96.

Lee, S.H., Sakai, E., Daimon, M., Bang, W.K., 1999. Characterization of fly ash directly collected from electrostatic precipitator. Cement Concrete Research 29, 1791-1797.

Lee, G.K., Whaley, H., 1983. Modification of combustion and fly-ash characteristics by coal blending. Journal of the Institute of Energy 56, 190-197.

Lester, E., Alvarez, D., Gawronski, E., Petersen, H., Rosenberg, P., Vleeskens, J., Kwiecińska, B., Misz, M., Pusz, S., Flores, D., Marques, M., Valentim, B., Panaitescu, C., Alonso, M.J., Gómez, A., Méndez, L.B., Stefanova, K., Barranco, R., Clift, D., Hanson, S., Thompson, A., Watts, D., 2000. Atlas of Char Occurrences of the Combustion Working Group-ICCP. CDrom.

Lester, E., Alvarez, D., Borrego, A.G., Valentim, B., Flores, D., Clift, D.A., Rosenberg, P., Kwiecińska, B., Barranco, R., Petersen, H.I., Mastalerz, M., Milenkova, K.S., Panaitescu, C., Marques, M.M., Thompson, A., Watts, D., Hanson, S., Predeanu, G., Misz, M., Wu, Tao, 2010. The procedure used to develop a coal char classification - Commission III Combustion Working Group of the International Committee for Coal and Organic Petrology. International Journal of Coal Geology 81, 333–342.

Lester, E., Cloke, M., Allen, M., 1996. Char characterization using image analysis techniques. Energy & Fuels 10, 696-703.

Lester, E., Cloke, M., Miles, N.J., 1993. The effect of operating conditions on char produced in a drop-tube furnace. Fuel Processing Technology 36, 101-108.

Li, J.J., Cui, J., Zhao, N.Q., Shi, C.S., Du, X.W., 2006. The properties of granular activated carbons prepared from fly ash using different methods. Carbon 44, 1298-1352.

Lightman, P., Street, P.J., 1968. Microscopical Examination of Heat Treated Pulverized Coal Particles. Fuel 47, 7-28.

Littlejohn, R.F., 1967. Pulverized-fuel combustion: swelling under rapid heating. J. Inst. Fuel 40, 128.

Lyer, R.S., Stanmore, B.R., 1995. Surface area of fly asdhes. Cement Concrete Research 25, 1403-1405.

McCrone, W.C., Delly, J.G. The Particle Atlas. 2nd Ed. Ann Arbor Science Publishers, MI, 1973, pp. 517, 544-549, 753 and 174-779.

Menéndez, R., Vleeskens, J.M., Marsh, H., 1993. The use of scanning electron microscopy for classification of coal chars during combustion. Fuel 72, 611-617.

Nandi, B.N., Brown, T.D., Lee, G.K., 1977. Inert coal macerals in combustion. Fuel 56, 125-130.

Newall, H.E., Sinatt, F.S., 1924. The carbonization of coal in the form of fine particles. I. The production of cenospheres. Fuel in Science and Practice, III, 12, 424-434.

Oka, N., Murayama, T., Matsuoka, H., Yamada, S., Yamada, T., Shinozaki, S., Shibaoka, M., Thomas, C.G., 1987. The influence of rank and maceral composition on ignition and char burnout of pulverized coal. Fuel Processing Technology 15, 213-224.

Petersen, H.I., 1998. Morphology, formation and palaeo-environmental implications of naturally formed char particles in coals and carbonaceous mudstones. Fuel 77, 1177-1183.

Phong-Anant, P., Salehi, M., Thomas, C., Baker, J., Conroy, A., 1989. In Proceedings of the 1989 International Conference on Coal Science, NEDO, Tokyo, 1989, p. 253

Ramsden, A.R., Shibaoka, M., 1982. Characterization and analysis of individual fly-ash particles from coal-fired power stations by a combination of optical microscopy, electron microscopy and quantitative electron microprobe analysis. Atmospheric Environment (1967) 16, 1982 pages 2191-2195, 2197-2206.

Rosenberg, P., Petersen, H.I., Sorensen, H.S., Thomsen, E., Guvad, C., 1996a. Combustion char morphology related to combustion temperature and coal petrography. Fuel 75, 1071-1082.

Rosenberg, P., Petersen, H.I., Sorensen, H.S., Thomsen, E., Guvad, C., 1996b. Combustion char characterisation. Final Report. Energy Research Project No. 1323/91-0012 and 1323/0018, Danmarks and Gronlands Geologiske Undersogelse Rapport, 1996/54, Copenhagen.

Sarbak, Z., Stanczyk, A., Kramer-Wachowiak, M., 2004. Characterisation of surface properties of various fly ashes. Powder Technology 145, 82-87.

Schure, M.R., Soltys, P.A., Natusch, D.F.S., Mauney, T., 1985. Surface area and porosity of coal fly ash. Environment Science Technology 19, 82-86.

Shibaoka, M., 1969a. An Investigation of the Combustion Processes of Single Particles. Journal of the Institute of Fuel 42, 59-66.

Shibaoka, M., 1969b. Combustion of coal in thin sections. Fuel 48, 285-295.

Shibaoka, M., 1985. Microscopic investigation of unburnt char in fly ash. Fuel 64, 263-269.

Shibaoka, M., Thomas, C. G., Young, B. C., Oka, N., Matsuoka, H., Tamara, K., Murayama, T., 1985. In Proceedings of the 1985 International Conference on Coal Science, Pergamon, Sydney, 1985, p. 665.

Shibaoka, M., Thomas, C.G., Gawronski, E., Young, B.C., 1989. A new concept in the microscopic classification of PF chars. In "1989 International Conference on Coal Science', NEDO, Tokyo, 1123-1126.

Sinnatt, F.S., Slater, L., 1922. Producer Gas from Pulverised Fuel. Fuel in Science and Practice (January), 2-3.

Sinnatt, F.S., McCullough, A.J. Newall, H.E., 1927. The carbonization of particles of coal. The study of cenospheres. Part 5. J. Soc. Chem. Ind. Transactions. London 46, 331-334.

Skorupska, N.M., Sanyal, A., Hesselman, G.J., Crelling, J.C., Edwards, I.A.S., Marsh, H., 1987. The use of an entrained flow reactor to assess the reactivity of coals of high inertinite content. Proceedings of the International Conference on Coal Science. Maastricht, The Netherlands, October 26-30, 1987, (edited by J.A. Moulijn, K.A. Nater, and H.A.G. Chermin), Elsevier, 827-831.

Snape, C.E., Smith, K.M., Arenillas, A., Drage, T.C., 2004. Comparison of two different approaches for enhancement of CO2 removal by adsorption on carbons. Prepr. Symp. Am. Chem. Soc., Div. Fuel Chem. 49, 685-687.

Street, P.J., Weight, R.P., Lightman, P. 1969. Further investigations of structural changes ocurring in pulverized coal particles during rapid heating. Fuel 48, 343-365.

Suárez-Ruiz, I., Hower, J.C., Thomas, G.A., 2006. Petrology and chemistry of fly ashes derived from the combustion of complex coal blends in Spanish power plants. Proceedings of International Coal Ash Technology Conference, AshTech 2006, Birmingham, UK, May 14-17, 2006; CD-rom.

Suárez-Ruiz, I., Hower, J.C., Thomas, G.A., 2007. Hg and Se capture and fly ash carbons from combustion of complex pulverized feed blends mainly of anthracitic coal rank in Spanish power plants. Energy Fuels 21, 59-70.

Suárez-Ruiz, I., Valentim, B., 2007. Fly ash components: A proposal for their identification and classification, Proceedings of World of Coal Ash Symposium, Covington, Kentucky, 7–10 May 2007, (CD publication). 8 pp.

Tang, L., Sheng, C., Gupta, R.P., Wall, T.F., 2005. The char structure characterization from the coal reflectogram. Fuel 84, 1268-1276.

Thomas, C.G., Gosnell, M.E., Gawronski, E., Phong-Anant, D., Shibaoka, M., 1993a. The behaviour of inertinite macerals under pulverised fuel (pf) combustion conditions. Organic Geochemistry 20, 779-788.

Thomas, C.G., Shibaoka, M., Gawronski, E., Gosnell, M.E., Brunckhorst, L.F., Phong-Anant, D., 1993b. Reactive (fusible) inertinite in pulverized fuel combustion. 1. A laser microreactor technique. Fuel 72, 907-912.

Tsai C.-Y., Scaroni A.W., 1984. Roles of various constituents in pulverised coal combustion. Meeting of Soc. of Mining Engineers of AIME, Denver, Colorado, 24-26 October.

Tsai, C.-Y., Scaroni, A.W., 1987a. Reactivity of bituminous coal chars during the initial stage of pulverized-coal combustion. Fuel 66, 1400-1406.

Tsai, C.-Y., Scaroni, A.W., 1987b. The structural changes of bituminous coal particles during the initial stages of pulverized-coal combustion. Fuel 66, 200-206

Valentim, B., Hower, J.C., Guedes, A., Flores, D., 2009. SEM/EDS of low-sulphur coal fly ash. International Journal of Energy for a Clean Environment 10(1-4), 147-166.

Valentim, B., Lemos de Sousa, M.J., Abelha, P., Boavida, D., Gulyurtlu, I., 2006. The identification of unusual microscopic features in coal and their derived chars: influence on coal fluidised bed combustion. International Journal of Coal Geology 67, 202-211.

Valentim, B., Guedes, A., Rodrigues, S., Flores, D., 2011. Case study of igneous intrusion effects on coal nitrogen functionalities. International Journal of Coal Geology 86, 291-294.

Valentim, B., Rodrigues, S., Ribeiro, S., Pereira, G., Guedes, A., Suárez-Ruiz, I., 2013. Relationships between the optical properties of coal macerals and the chars resulting from fluidized bed pyrolysis, International Journal of Coal Geology 111, 80-89.

Vleeskens, J.M., Malechaux, L., 1986. Characterization of Coal Combustion Residues. Stichting Energy Centre Netherlands (Publ. ref. ECN - 86 - 105).

Vleeskens, J.M., Nandi, N., 1986. Burnout of coals. Comparative bench-scale experiments on pulverized fuel and fluidized bed combustion. Fuel 65, 797-802.

Vleeskens, J.M., van Haasteren, T.W.M.B., Roos, M., Gerrits, J., 1988. Behaviour of different char components in fluidized bed combustion: a char petrography study. Fuel 67, 426-430.

Vleeskens, J.M., Menéndez, R.M., Roos, C.M., Thomas, C.G., 1993. Combustion in the burnout stage: the fate of inertinite. Fuel Processing Technology 36, 91-99.

Young, B.C., Thomas, C.G., Hamor, R.J., Banas, E., Shibaoka, M., Matsuoka, H., Yamada, S., 1987. The effects of maceral composition and rank in coal combustion. In Extended Abstracts, Joint Fall Meeting, Western States and Japanese Sections, The Combustion Institute, Pittsburgh, 119-121.

Yu, J., Lucas, J.A., Wall, T.F., 2007. Formation of the structure of chars during devolatilization of pulverized coal and its thermoproperties: A review. Progress in Energy and Combustion Science 33, 135-170.

Fig. 1

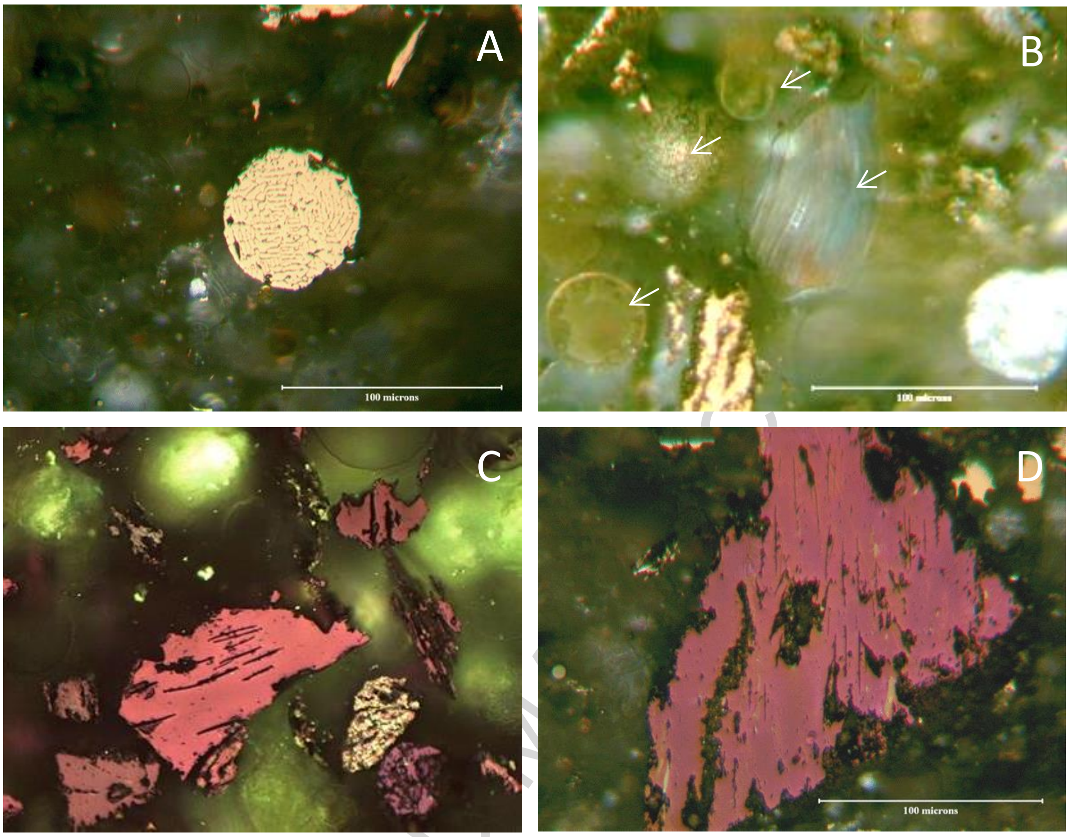


Fig. 2

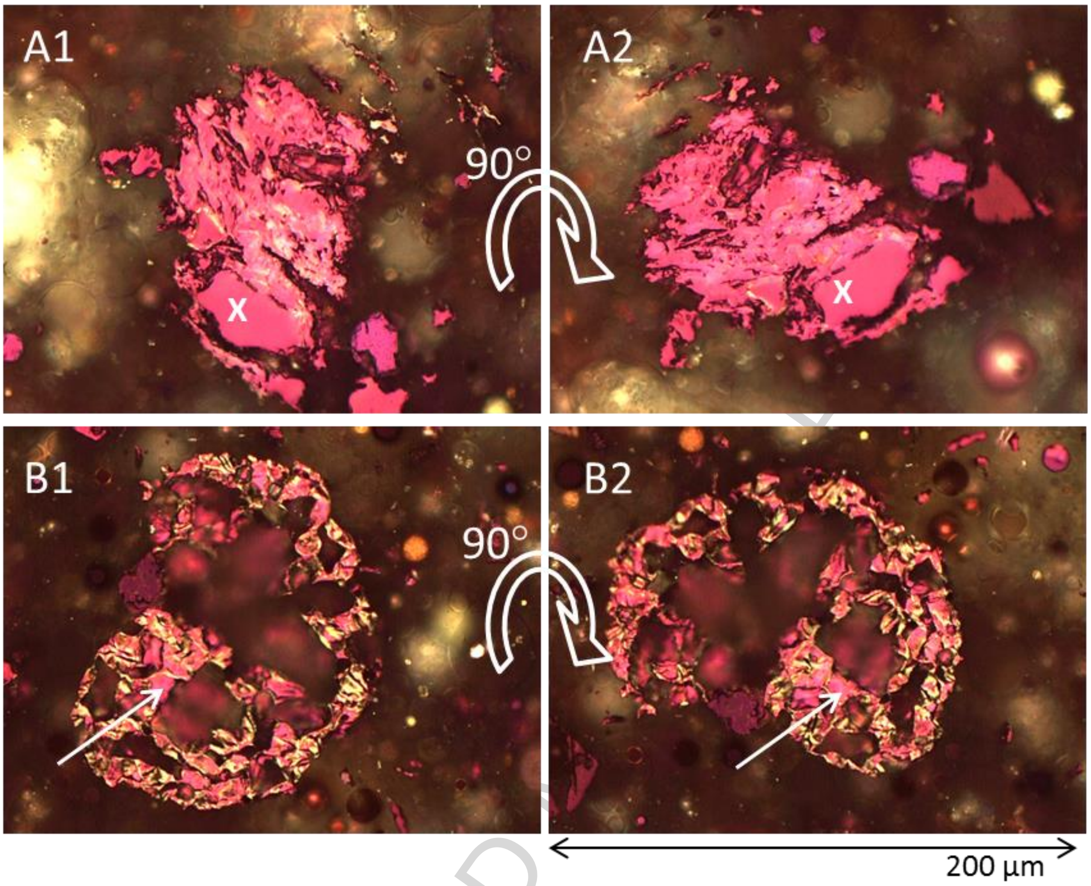


Fig. 3

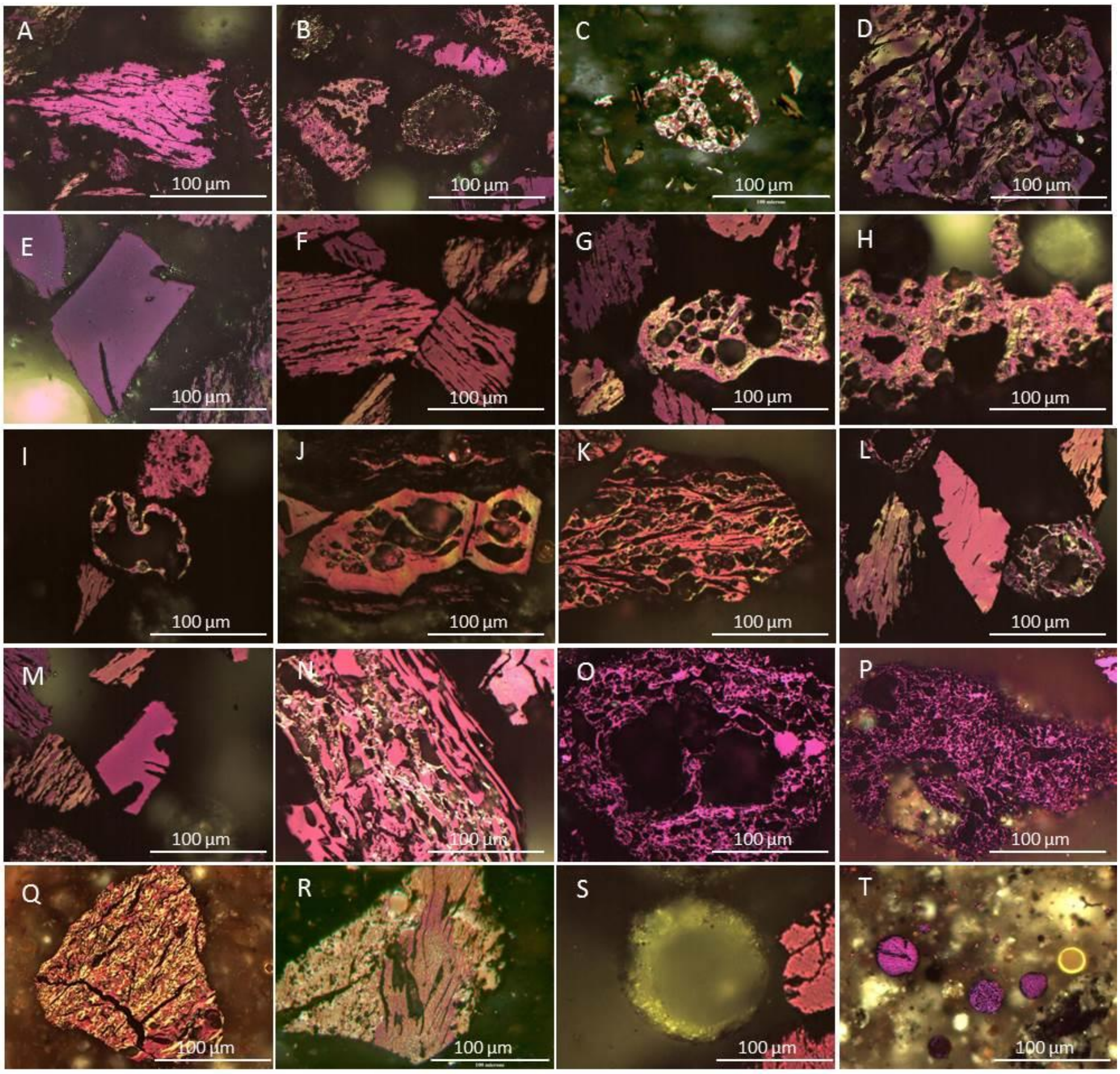

A
100 µm
B
100 µm
C
100 µm
D
100 µm
E
100 µm
F
100 µm
G
100 µm
H
100 µm
I
100 µm
J
100 µm
K
100 µm
L
100 µm
M
100 µm
N
100 µm
O
100 µm
P
100 µm
Q
100 µm
R
100 µm
S
100 µm
T
100 µm

Fig. 4

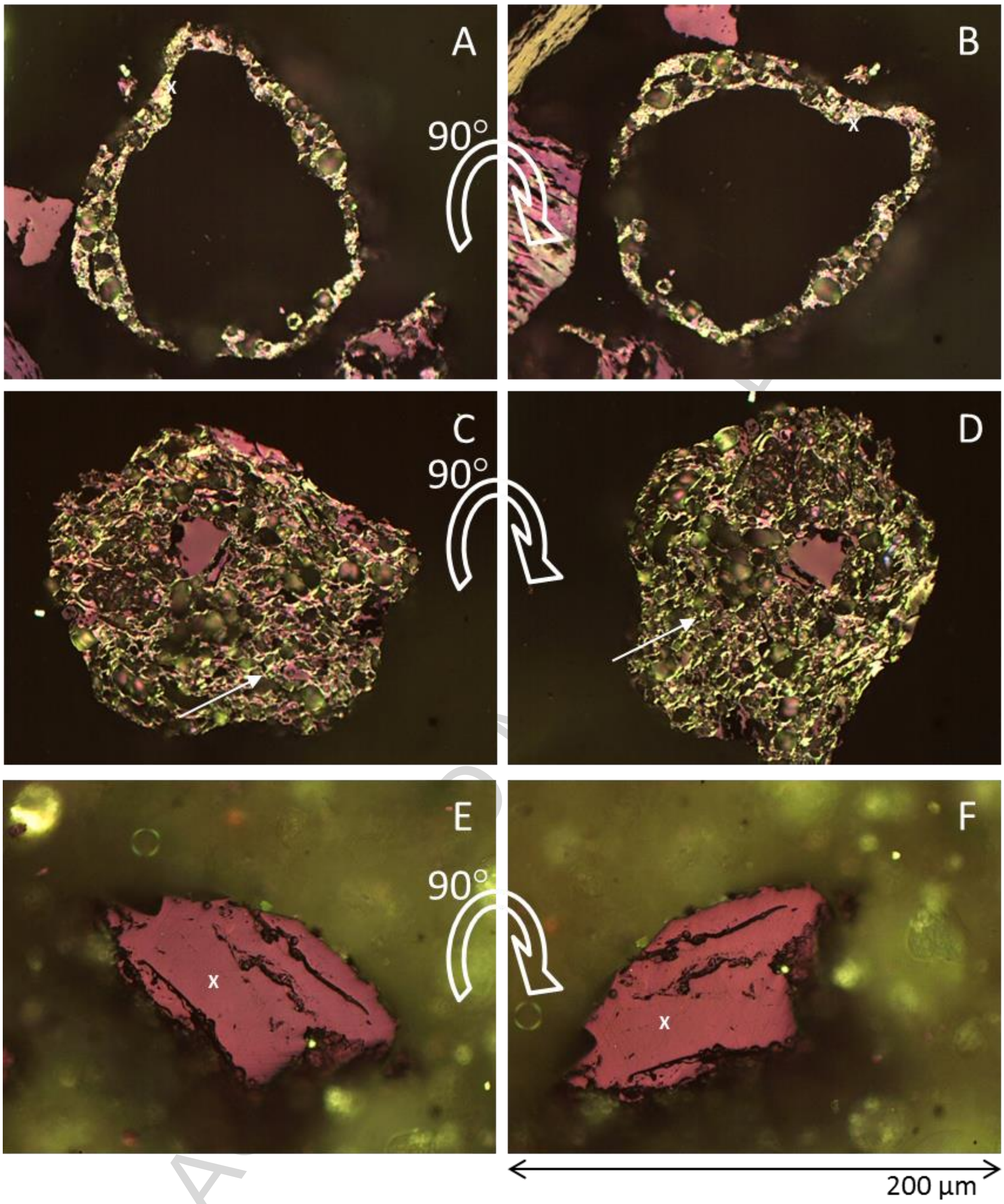


Fig. 5

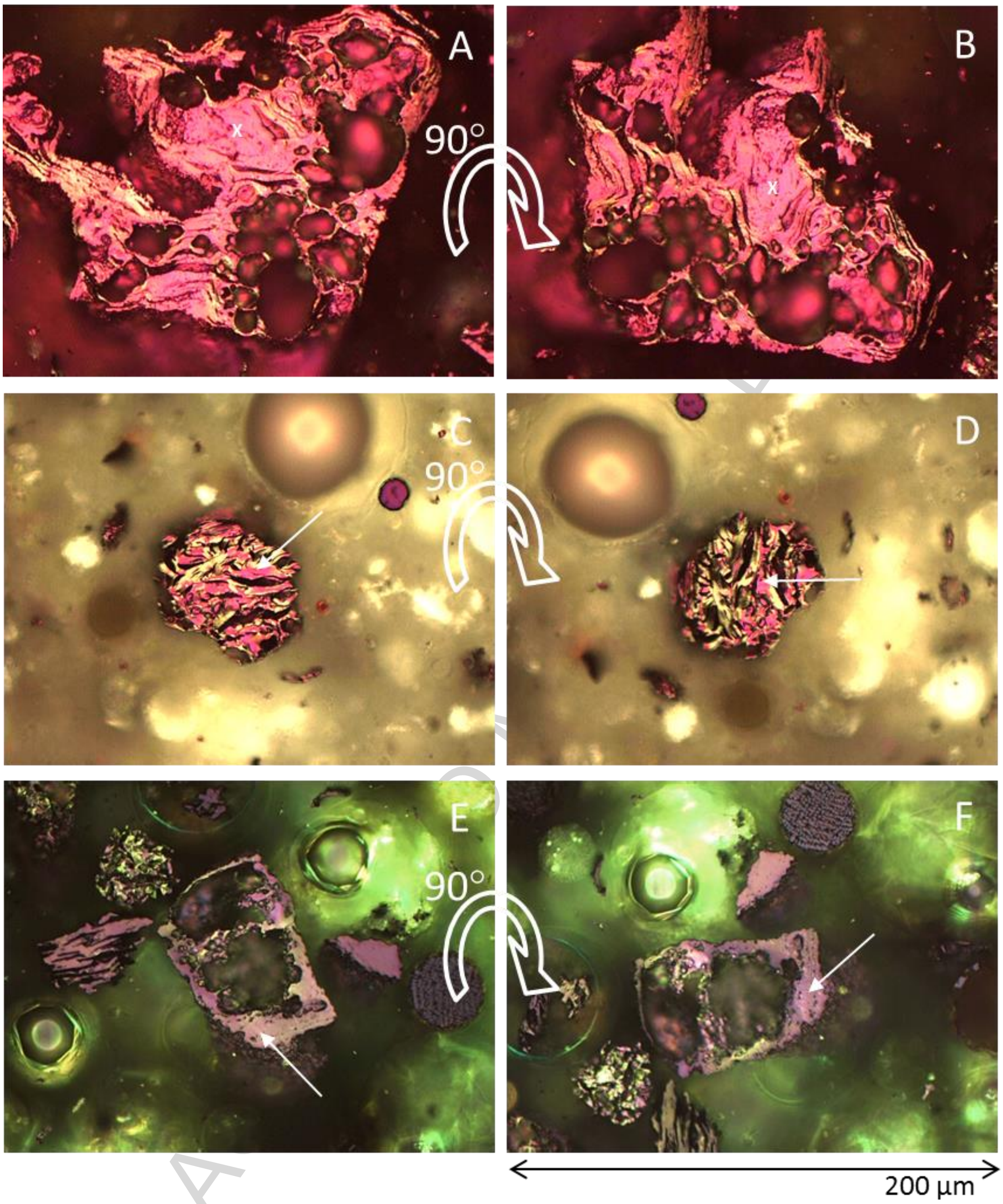


Fig. 6

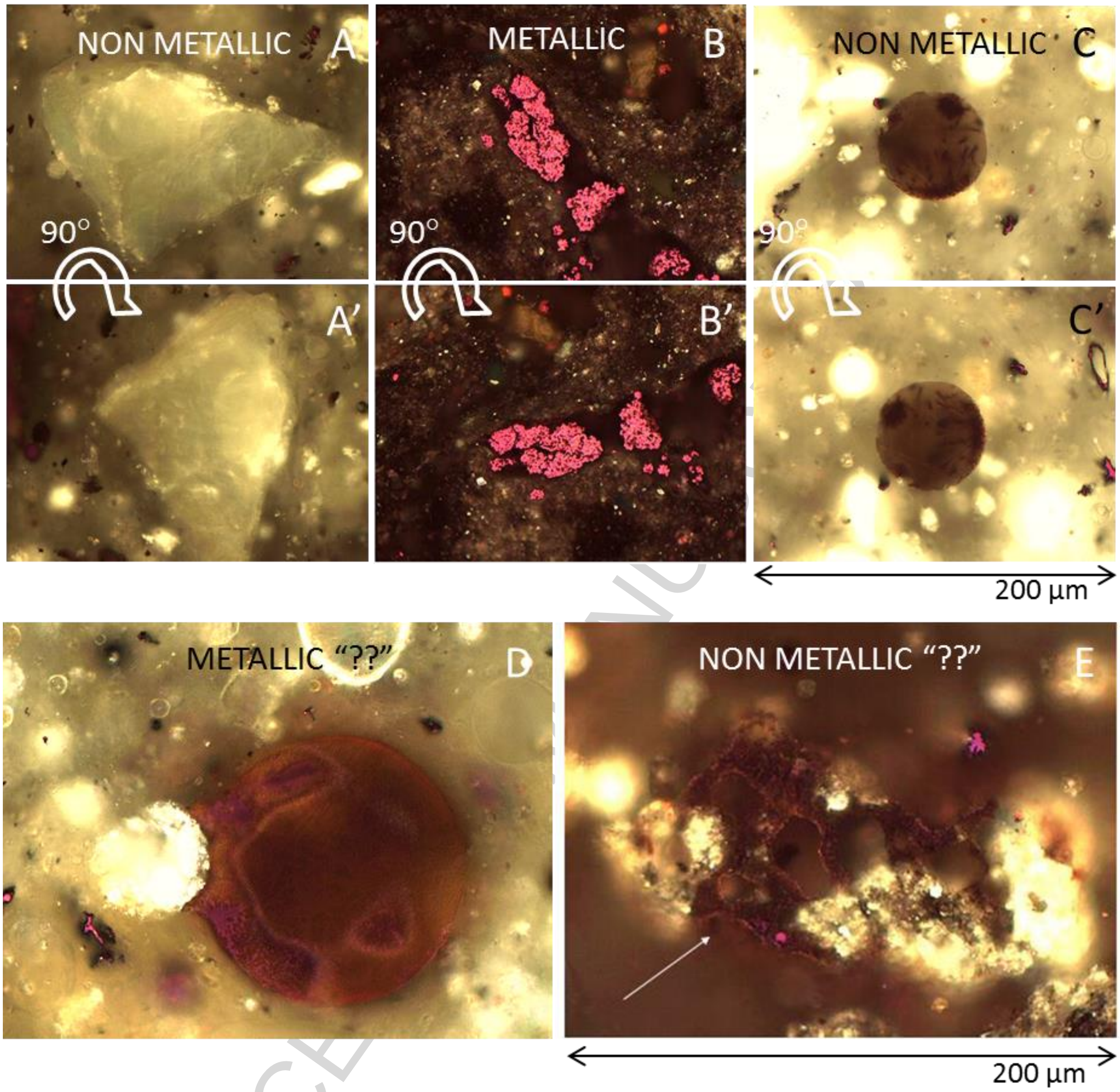

NON METALLIC
A
METALLIC
B
NON METALLIC
C
90°
90°
90°
A'
B'
C'
200 µm
METALLIC "??"
D
NON METALLIC "??"
E
200 µm

Fig. 7

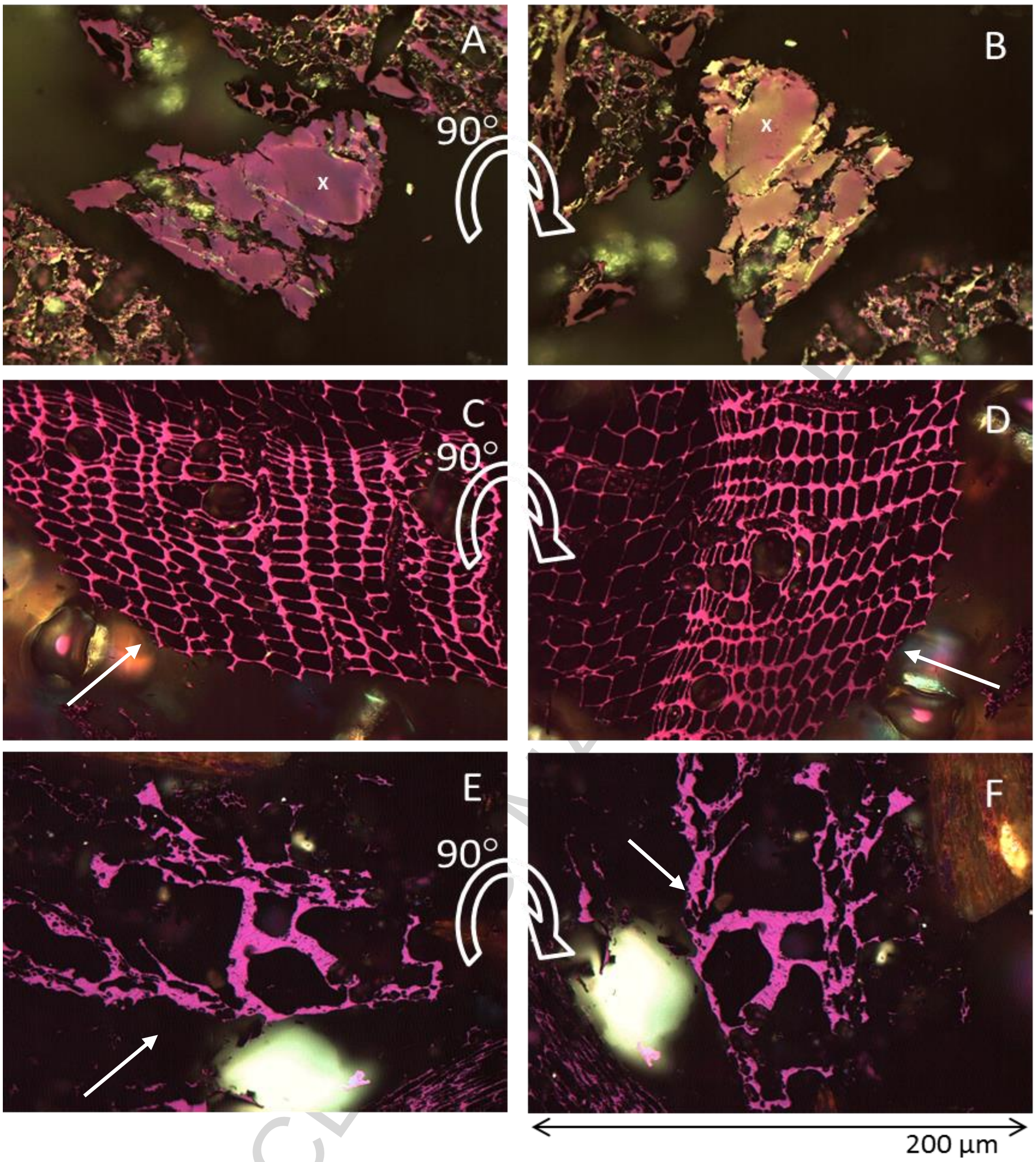
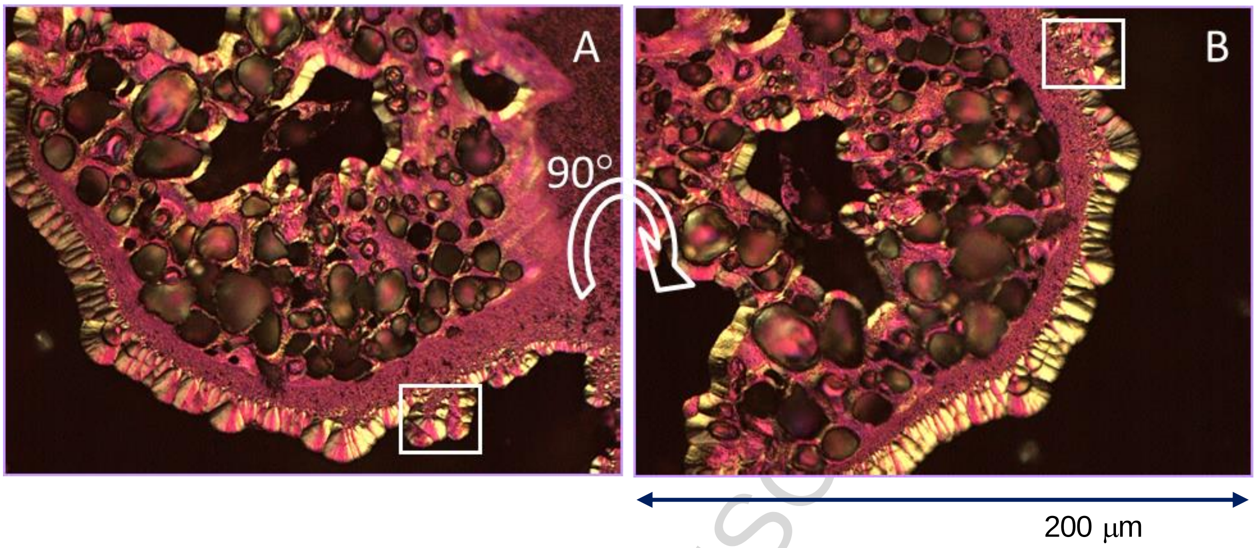


Fig. 8



Level # 1: whole particle: Organic
Level # 2: particle surface identification: Fused
Level # 3: particle surface identification: Dense
Level # 4: particle surface identification: Anisotropic
Level # 5: whole particle: Coal

Fig. 9

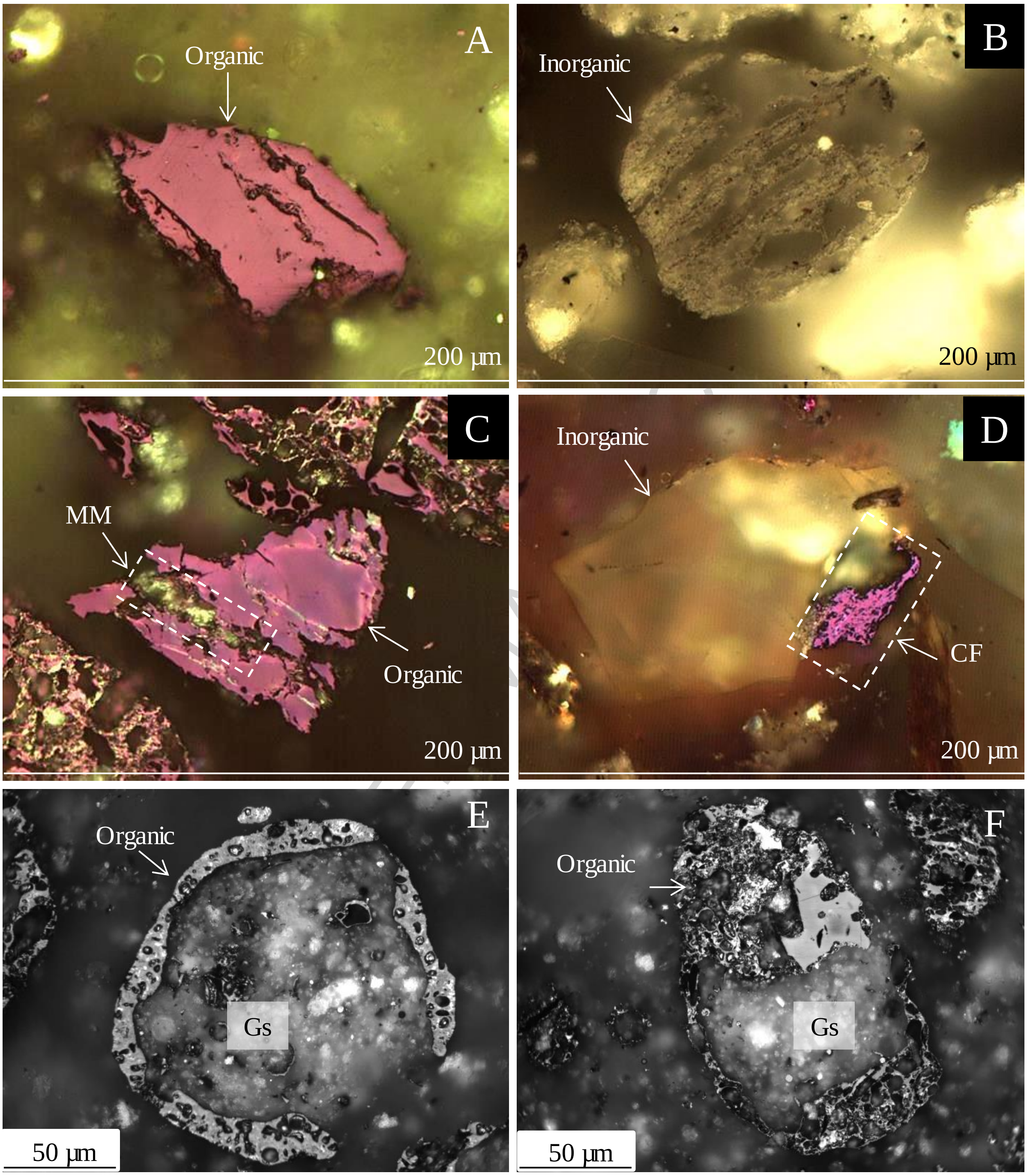

A
Organic
200 µm
B
Inorganic
200 µm
C
MM
Organic
200 µm
D
Inorganic
CF
200 µm
E
Organic
Gs
50 µm
F
Organic
Gs
50 µm

Figure Captions:

Fig. 1. Optical microscopy photomicrographs. These and all photomicrographs were taken with oil immersion objective of ×50, polarized light, and 1 λ retarder plate. Examples of mineral matter and inertoids: A) spinel; B) non-metallic mineral matter (arrows); C) inertoid; D) inertoid derived from anthracitic vitrinite. (Long side of the image is ~200 microns)

Fig. 2. Example of images of the first fly-ash classification round robin exercise using the cross and arrow pointing system.

Fig. 3. Examples of unburned carbons in fly-ash: A) anisotropic unfused from vitrinite; B) anisotropic fused from vitrinite; C) anisotropic from pet coke; D) anisotropic from inertinite; E) isotropic unfused from inertinite; F) massive, anisotropic, unfused from high rank (anthracite) vitrinite; G) porous, anisotropic, fused from high rank (semi-anthracite) vitrinite; H) porous, anisotropic, fused from high rank (semi-anthracite) vitrinite; I) porous, anisotropic, fused from medium rank vitrinite; J) porous, vesiculated, anisotropic, fused from inertinite; K) porous, vesiculated, anisotropic, partially fused from Inertinite; L) massive, isotropic from high rank (anthracite) vitrinite; M) massive, isotropic, unfused from inertinite; N) isotropic, unfused from inertinite retaining the original structure.; O) porous, isotropic, fused from low-rank vitrinite; P) porous, isotropic, fused from low-rank coal; Q) Petroleum coke, anisotropic; R) Natural coke, anisotropic; S) glassy material; T) spinels (purple spheres) and glassy material (yellow sphere).

Fig. 4. Fly-ash components, 2007 exercise results. Examples of 80 to 100 % level of agreement (Table 3) for the four criteria: A-B and C-D): anisotropic, fused, porous particle from coal; E-F): isotropic, unfused, dense particle from coal.

Fig. 5. Fly-ash components, 2007 exercise results. Examples of < 50 % level of agreement for the four criteria (Table 3): A-B): anisotropic "??", unfused "??", dense particle from coal; C-D): anisotropic, fused "??", porous "??" particle from coal "??"; E-F): anisotropic "??", fused "??", porous particle from coal.

Fig. 6. Inorganic components in fly-ash, 2007 exercise results. Examples of % level of agreement for the metallic or non-metallic category (see agreement classes in Table 3): A, B and C): 80-100 %; D and E): examples of < 50 %.

Fig. 7. Organic components in fly-ash, 2009 exercise results. Examples of 80-100 % level of agreement (Table 4) in the marked field: A-B): anisotropic, unfused, and dense particle section from coal; C-D): isotropic, unfused, and porous particle from biomass; E-F): isotropic, fused, and porous particle from biomass.

Fig. 8. Fly-ash components, 2011 exercise results. Example of high level of agreement (> 80%) for the five levels considered: A-B): organic, fused, dense, and anisotropic particle from coal (the rim is pyrolytic carbon).

Fig. 9. Level #1, "nature": A) Organic: 100% carbonaceous matter; B) Inorganic: 100% mineral matter (partially baked clay); C) Organic: carbonaceous particle (inertoid) with less than <50% mineral matter (MM); D) Inorganic: particle > 50% mineral matter (quartz) with a char/carbonaceous fragment (CF) attached; E) Organic: char cenosphere filled with glassy spheres as inorganics (Gs); F) Organic: char filled with glassy spheres inorganics (Gs).

Table 1. Glossary of pre-classification categories of microscopic components identified in fly-ash.

Organic fraction

The organic fraction includes fly-ash carbons (anisotropic and isotropic unburned carbons) exclusively derived from coal combustion (combustion of coal macerals), and particles classified as " other organics" which are carbons from petroleum coke, natural coke, and unburned coal fragments. This last category can be composed of either anisotropic or isotropic carbons.

Unburned carbons exclusively derived from coal (macerals) combustion

(i) Anisotropic

1) Porous and vesiculated particles from the combustion of vitrinite of semi-anthracite and bituminous coal rank: Fused particles, porous and strongly vesiculated particles, developing a spherical hollow structure (the carbon cenosphere) or a network-like structure with few chambers. These carbons develop diverse coke anisotropic domains depending on the coal rank. SEM images of these fly ash carbons usually show perforated spheres.

2) Massive particles derived from the combustion of vitrinite of anthracitic/meta-anthracitic coal rank: Unfused particles, with an homogeneous and uniform anisotropy, may show some cracks and very small porosity in the majority of the cases although the porosity cannot always be detected by optical microscopy. SEM images of these fly-ash carbons show unfused particles of variable and irregularly distributed porosity. These carbons show an angular and irregular morphology.

3) Porous and vesiculated particles from the combustion of inertinites: Fused or partially fused particles, irregularly porous and vesiculated, with cracks, developing a network-like structure. These carbons are anisotropic to strongly anisotropic. However, they show a sweeping anisotropy totally different to that shown by the other anisotropic fly ash carbons.

4) Massive particles from inertinite combustion: Relatively massive particles, partially fused with a low porosity.

5) Undifferentiated anisotropic fragments: Small anisotropic carbons, less than 10-15 µm, which cannot be assigned to any of the previously described categories of carbons.

(ii)Isotropic

1) Porous and vesiculated particles from the combustion of vitrinite of low rank coals: Fused particles, vesiculated and porous developing structures like cenospheres and networks.

2) Massive particles derived from the combustion of inertinite: Totally isotropic particles, unfused or partially fused with variable porosity.

3) Particles from inertinite retaining their original structure: Unfused particles with partially to well-preserved original structure.

4) Undifferentiated isotropic fragments: Small isotropic particles smaller than 10-15 µm, massive, irregular or vesiculated, that cannot be assigned to any of the previously described categories.

(iii) Unburned and/or oxidized coal particles: *Mainly isotropic particles if derived from bituminous coal rank. Various macerals can be identified: vitrinite, liptinite or inertinite.*

Other organics (*i.e.*, carbons which are not derived from coal combustion).

1) Particles from pet coke.

2) Particles from natural coke: found in fly ashes derived from combustion of very high rank coals.

3) Particles from tires: anisotropic particles, irregular, massive or vesiculated.

Inorganic fraction

Categories defined in Hower and Mastalerz (2001) and Hower et al. (2005) including glassy material (that is alumino-silicates with smaller amounts of Fe, Ca, and other elements), quartz, oxides, mullite, spinels, sulfides, sulphates, and " other mineral matter" (inorganic matter that, because of its size and / or the microscope resolution cannot be clearly identified and assigned to any of the other described categories of inorganic components).

Table 2. ICCP 2006-2007 fly-ash classification (established in 2006 at the 58th ICCP meeting).

<table>
<tr><th rowspan="2"></th><th rowspan="2">Nature</th><th rowspan="2">Optical texture</th><th rowspan="2">Character</th><th rowspan="2">Structure / Morphology</th><th colspan="2">Origin</th></tr>
<tr><th>Coal</th><th>Other</th></tr>
<tr><td rowspan="11">FLY-ASH COMPONENTS</td><td rowspan="8">Organic Fraction (Fly-Ash Carbons)</td><td rowspan="4">Unburned Carbons Anisotropic Components</td><td rowspan="2">Fused Carbons</td><td>Dense / Massive</td><td rowspan="8">Low, Medium and High rank coals; Specific burned maceral; Unburned coal; Natural coke</td><td rowspan="8">Pet coke, Tires, Natural coke; etc.</td></tr>
<tr><td>Porous / Vesiculate</td></tr>
<tr><td rowspan="2">Unfused Carbons</td><td>Dense / Massive</td></tr>
<tr><td>Porous / Vesiculate</td></tr>
<tr><td rowspan="4">Unburned Carbons Isotropic Components</td><td rowspan="2">Fused Carbons</td><td>Dense / Massive</td></tr>
<tr><td>Porous / Vesiculate</td></tr>
<tr><td rowspan="2">Unfused Carbons</td><td>Dense / Massive</td></tr>
<tr><td>Porous / Vesiculate</td></tr>
<tr><td rowspan="3">Inorganic Fraction</td><td rowspan="3"></td><td>Metallic</td><td rowspan="3"></td><td colspan="2" rowspan="3">Composition*: Glassy material (Alumino-silicates); Quartz; Oxides and hydroxides (Fe, Ca); Mullite; Spinels; Sulfides (rare, with unburned coal); Sulfate; Other inorganics.</td></tr>
<tr><td>Non- metallic</td></tr>
<tr><td>Undifferentiate component</td></tr>
</table>

*Hower et al. (2005).

Table 3. Results of the first ICCP round robin exercise (year 2007) on fly-ash classification.

Analysts' performance

Analyst number	A1	A2	A3	A4	A5	A7	A10	A11	A12	A14	A15	A17	Average	Median	Mode
Optical Texture (%)	89	80	86	90	83	72	77	77	75	83	85	90	82	83	90
Character (%)	81	79	79	87	71	66	79	73	63	69	81	71	75	76	79
Structure (%)	86	86	85	89	85	84	92	89	77	84	78	79	85	85	86
Origin (%)	97	94	91	91	92	90	94	62	97	93	86	93	90	93	97
Total Organic Fraction (%)	88	85	85	89	83	78	86	75	78	82	83	83	83	83	83
Total Inorganic Fraction (%)	73	70	73	95	80	70	62	78	47	65	78	82	73	73	73
Analyst Total (%)	85	82	83	90	82	76	81	76	72	79	82	83	81	82	82

Amount of particles assigned to each qualifier

	Anisotropic	Isotropic	Fused	Unfused	Partially Fused	Massive	Porous	Coal	Others	Metallic	Non-Metallic	Undifferentiated
Optical Texture	56	44										

(%)											
Character (%)	------------------	40	31	29							
Structure (%)		----------------------			47	53					
Origin (%)					--------------		88	12			
Inorganic Fraction (%)							--------------		38	48	14

Agreement classes

Optical Texture		Character		Structure		Origin		Inorganic Fraction	
%	%	%	%	%	%	%	%	%	%
≥50 <65	10	<50	5	≥50 <65	13	≥50 <65	1	<50	3
≥65 <80	25	≥50 <65	31	≥65 <80	15	≥65 <80	8	≥50 <65	27
≥80 ≤100	65	≥65 <80	29	≥80 ≤100	72	≥80 ≤100	91	≥65 <80	40
		≥80	35					≥80	30

Table 4. Results of the second ICCP round robin exercise (year 2009) on fly-ash classification.

Analysts' performance

Analyst number	A1	A2	A3	A4	A5	A7	A10	A12	A14	A15	A17	A18	Average	Median	Mode
Optical Texture (%)	82	81	84	91	93	85	85	87	94	75	92	94	87	86	85
Character (%)	90	79	70	87	76	72	81	90	72	88	78	92	81	80	90
Structure (%)	70	62	73	73	55	78	68	48	70	74	73	76	68	72	73
Origin (%)	95	82	79	78	92	76	93	86	84	85	95	95	87	86	95
Total Organic Fraction (%)	84	76	77	82	79	78	82	78	80	81	85	89	81	80	78
Total Inorganic Fraction (%)	92	97	95	89	87	84	89	54	76	82	80	87	84	87	89
Analyst Total (%)	86	80	80	83	80	79	83	73	79	81	83	89	81	81	80

Amount of particles assigned to each qualifier

	Anisotropic	Isotropic	Fused	Unfused	Partially Fused	Massive	Porous	Coal	Biomass	Others	Metallic	Non-metallic	Undifferentiated
Optical Texture	49	51											

(%)												
Character (%)	-------------------	56	44	0								
Structure (%)			-----------------------		55	45						
Origin (%)						---------------	72	26	2			
Inorganic Fraction (%)								----------------------		35	64	1

Agreement classes

Optical Texture %	%	Character %	%	Structure %	%	Origin %	%	Inorganic Fraction %	%
≥50 <65	5	<50	1	≥50 <65	19	<50	2	<50	2
≥65 <80	18	≥50 <65	17	≥65 <80	24	≥50 <65	8	≥50 <65	14
≥80 ≤100	77	≥65 <80	28	≥80 ≤100	57	≥65 <80	17	≥65 <80	21
		≥80	54			≥80	73	≥80	63

Table 5. Fly-Ash Working Group. Classification of Fly-Ash Components: proposed for the 2011 exercise.

<table>
<tr><th></th><th>Level #1
Nature</th><th>Level #2
Character</th><th>Level #3
Structure / Morphology</th><th>Level #4
Optical texture</th><th>Level #5
Origin</th><th>Level #6
Type of particle</th></tr>
<tr><td rowspan="8">Fly-ash components</td><td rowspan="8">Organic fraction (fly-ash carbons)</td><td rowspan="4">Fused</td><td rowspan="2">Dense / Massive</td><td>Isotropic</td><td rowspan="8">Coal
Biomass
Pet coke
Other</td><td rowspan="8">Apply the ICCP Char Classification *</td></tr>
<tr><td>Anisotropic</td></tr>
<tr><td rowspan="2">Porous / Vesiculate</td><td>Isotropic</td></tr>
<tr><td>Anisotropic</td></tr>
<tr><td rowspan="4">Unfused</td><td rowspan="2">Dense / Massive</td><td>Isotropic</td></tr>
<tr><td>Anisotropic</td></tr>
<tr><td rowspan="2">Porous / Vesiculate</td><td>Isotropic</td></tr>
<tr><td>Anisotropic</td></tr>
<tr><td></td><td colspan="6">Inorganic fraction</td></tr>
</table>

*Lester et al. (2000, 2010)

Table 6. Results of the third ICCP round robin exercise (year 2011) on fly-ash classification.

Analysts' performance

Analyst number	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	Average	Median	Mode
Nature (%)	100	96	100	92	100	88	96	92	100	96	92	96	100	96	96	100
Character (%)	72	68	60	28	68	60	80	64	68	64	80	44	72	62	64	60
Structure (%)	72	68	68	56	72	80	52	84	76	92	76	52	72	70	72	72
Texture (%)	80	80	92	68	80	68	72	84	80	80	80	80	72	78	80	80
Origin (%)	64	64	64	60	48	52	56	60	52	68	60	48	60	56	56	60
Analyst Total (%)	78	75	77	61	74	70	71	77	75	80	78	64	75	72	75	75

Amount of particles assigned to each qualifier

	Inorganic	Organic	Fused	Unfused	Dense	Porous	Isotropic	Anisotropic	Coal	Biomass	Others
Nature (%)	20	80									
Character (%)			50	50							
Structure (%)					42	58					
Texture (%)							38	62			
Origin (%)									48	36	16

Agreement classes

Nature		Character		Structure		Texture		Origin	
%	%	%	%	%	%	%	%	%	%

≥50 <65	4	<50	0	≥50 <65	20	≥50< 65	20	<50	4
≥65 <80	0	≥50 <65	24	≥65 <80	36	≥65< 80	12	≥50 <65	28
≥80 ≤100	96	≥65 <80	40	≥80 ≤100	44	≥80≤ 100	68	≥65 <80	36
		≥80	36					≥80	32

Table 7. Group mean and standard deviation of the various classification criteria.

		Group Mean	Standard deviation
Nature	Inorganic	4.54	1.127
	Organic	20.46	1.127
Character	Fused	12.31	5.186
	Unfused	9.15	3.955
Structure	Dense	11.85	3.976
	Porous	11.00	3.416
Optical Texture	Isotropic	10.54	2.602
	Anisotropic	12.31	2.175
Origin	Coal	12.38	3.709
	Biomass	4.15	1.281
	Other	4.85	3.184

Table 8. Accuracy and bias of results calculated against the group mean and standard deviation for the various classification criteria.

Analysts	Nature		Character		Structure		Optical Texture		Origin					
	Inorganic	Organic	Fused	Unfused	Dense	Porous	Isotropic	Anisotropic	Coal	Biomass	Other			
	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	SMSD*	AUMSD**	ASMSD***	Bias
#1	0.410	-0.410	0.326	-0.797	-0.213	-0.586	-0.976	-0.141	0.166	0.661	-0.894	0.507	-0.223	Low
#2	-0.478	0.478	-0.638	0.973	1.045	-1.171	0.946	-0.601	0.975	-0.120	0.048	0.679	0.132	Low
#3	0.410	-0.410	1.869	-1.556	1.799	-1.464	-0.591	1.698	0.436	-0.901	-0.580	1.065	0.065	Low
#4	-0.478	0.478	-1.023	-0.545	0.542	0.878	-0.591	-0.141	-0.104	-0.120	0.048	0.450	-0.096	Low
#5	0.410	-0.410	0.133	-0.545	0.290	-1.171	-0.976	-0.141	-1.721	-0.120	1.618	0.685	-0.239	Low
#6	-2.253	2.253	-0.831	1.225	0.039	0.586	1.715	-1.981	-0.643	-0.120	-0.580	1.111	-0.054	Low
#7	-0.478	0.478	0.133	-0.292	-2.225	2.049	-1.744	1.238	0.975	-1.681	-0.894	1.108	-0.222	Low
#8	-1.366	1.366	-0.831	1.225	-0.213	0.293	0.177	-0.141	0.166	1.441	-0.894	0.737	0.111	Low
#9	0.410	-0.410	1.098	-1.050	-0.213	0.293	-0.207	0.318	0.436	-0.120	0.362	0.447	0.083	Low
#10	1.297	-1.297	0.519	0.214	-0.213	0.878	1.330	-0.601	0.436	1.441	-1.208	0.858	0.254	Low
#11	0.410	-0.410	0.905	-0.292	0.793	-0.293	0.562	0.318	1.514	-1.681	0.048	0.657	0.170	Low
#12	1.297	-1.297	-1.795	1.731	-1.219	0.293	-0.207	1.238	-1.721	0.661	0.990	1.132	-0.003	Low
#13	0.410	-0.410	0.133	-0.292	-0.213	-0.586	0.562	-1.061	-0.913	0.661	1.932	0.652	0.020	Low

* Signed multiple of the standard deviation (SMSD);
** Mean of the sum of the unsigned multiples of the standard deviation (AUMSD), it is a measure of accuracy;
*** Mean of the signed multiple of the standard deviation (ASMSD), it is an indicator of bias.

Highlights

- Development of a petrographic classification of fly-ash components from coal combustion and co-combustion.
- It is an ICCP Classification System, developed by the Fly-Ash Working Group – Commission III
- The classification system developed is based on a small number of microscopic criteria, subdivided into six independent levels / categories
- Three levels of the classification are directed at the whole particle identification on the basis of nature, origin and type of fly-ash particle.
- The other three levels are directed at the smaller field section identification on the basis of character, structure and optical texture of unburned carbons.
- Inorganic components of the fly-ash, are classified according to their composition in terms of metallic / non-metallic character.